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BORON, BORON HYDRIDES, AND THEIR DERIVATIVES.

B O R O N.

5	
B	3
10.82	2

Boron [6], being one of the elements in the upper series of the third group of the periodic system of elements, appears to be the first element to reveal principally nonmetallic properties. At the same time, being an element of the third group, boron possesses properties which make it similar to elements of the major subgroups of the right side of the periodic system.

Boron has several valencies: it can be principally trivalent, tetravalent coordinately, and pentavalent formally. Boron often forms compounds which do not agree with ordinary concepts of chemical valency. This is depicted in complex formulas of boranes, and consequently in formulas of metal borides. Indeed, formulas of borides are characteristic for their great complexity. Some of them have atomic composition of defined compounds

$$B_6Me \ , \ B_{12}Me \ , \ B_2Me \ ,$$

typical for crystals of intermetallic compounds of transition metals, and at the same time, among metal - boron systems, there are many phases of variable composition which chemically, are not yet defined.

Boron belongs to elements which are relatively common [8]. Its content in the earth's crust is

$$5 \cdot 10^{-4}$$

percent. In pure form, it can be prepared from boric acid:

$$B_2O_3 + 3Mg \ = \ 3MgO + 2B + 102 \text{ kcal}$$

After removal of MgO with HCl we obtain elementary boron as a dark brown powder.

Purest elementary boron was prepared by the thermal decomposition of BBr_3 vapors on a tantalum wire electrically heated to 1500°.

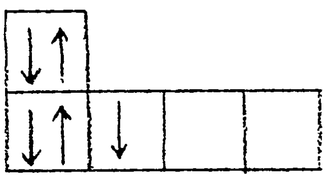
Its sp.gr. = 2.3

m.p. = 2075°

b.p. = 2550°.

Chemical bond and molecular structure [11]

The distribution of electrons can be shown by the following patterns:



s p

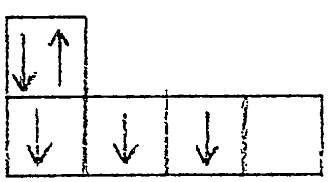
$1s^2 2s^2 2p$

and

K	L	
1s	2s	2p
2	2	1

In a boron atom, one of the 2s-electrons can shift to a free 2p-cell. Such a transition to the excited state with separation of an electron pair by passage of one electron to the next level is shown by the following pattern:

1s



2s 2p

B* $1s^2 2s 2p^2$

The excited B atom has 3 unpaired electrons, therefore it is trivalent. Energies of electron bonds in atoms can be expressed by ionization

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potentials, which give the energy of electron emission from an atom. Ionization potentials reveal a series of interesting regularities, since they are, to a certain degree, connected with chemical properties, e.g., the tendency to form ionic compounds. An unpaired s-electron is forced out easier than a pair. This means, that the pairing of two electrons in the s-cell increases the bond strength. A p-electron appears to be weaker than one of the paired s-electrons.

Ionization potentials of various orders. [11] Table 1.

	external electrons	I_1	I_2	I_3	I_4	I_5	electron affinity kcal
B	s^2p	0.61	1.85	2.8	19.3	25	3

Chemical valency.

Boron, by losing one electron, can be a nullvalent ($1s^22s^2$) or bivalent ($1s^22s2p$) positive ion. The formation of bivalent B^+ requires additional energy for splitting two 2s-electrons:

$$1s^22s^2 \longrightarrow 1s^22s2p.$$

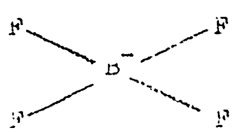
The double-charge positive B^{++} is univalent ($1s^22s$). The B^{+++} of Kossel' is nullvalent and obviously hardly probable.

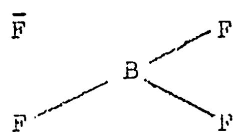
By gaining one electron boron becomes, like carbon, a tetravalent ion with one negative charge:

$$1s^22s2p^3.$$

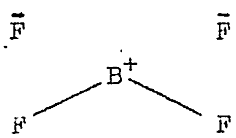
Compounds of this type are very well known (e.g. BH_4^- in $LiBH_4$).

In $H^+(BF_4)^-$ the ion BF_4^- has the following structure:

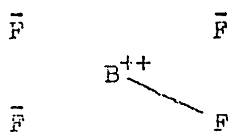




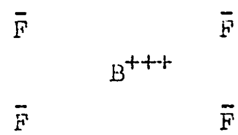
four structures



six structures

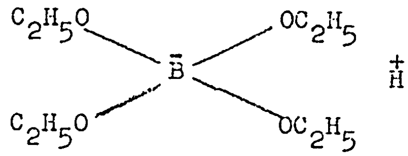


four structures, small weight



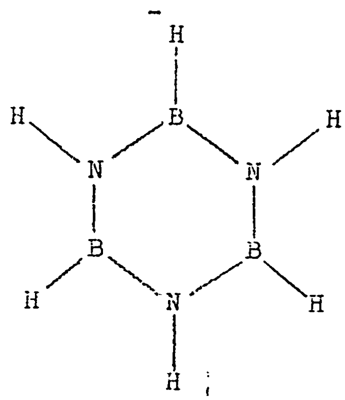
one structure with very small weight

Boric acid esters $B(OC_2H_5)_3$ easily and rapidly react with alcohols forming alcohol acids which do not differ from ordinary organic acids and give stable salts. They have the following structure:

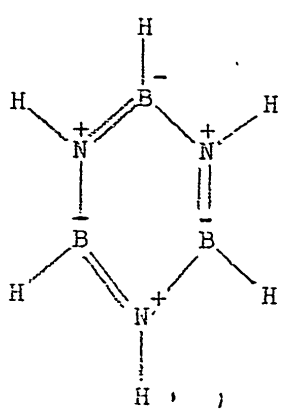


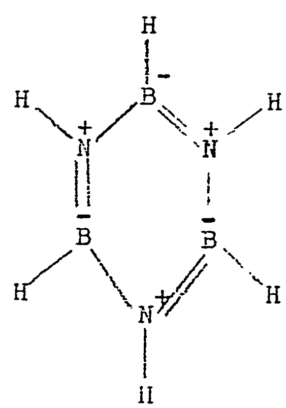
The negative charge is not localized at the B atom, but can be placed at the oxygen atoms.

The existence of tetravalent positive N and tetravalent negative B makes a series of combinations possible. In "inorganic benzene" $B_3N_3H_6$, next to the homeopolar structure



are given ionic structures with tetravalent positive N and tetravalent negative B. Here we have two structures of the Kekule type





Distance B — N = 1.44 Å. Due to the fact that the linkage is partly double, this distance is noticeably shortened in comparison

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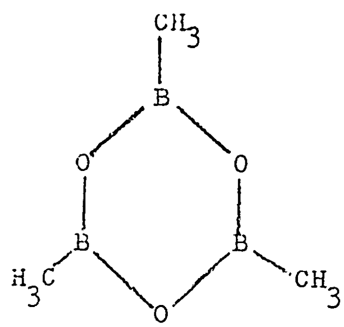
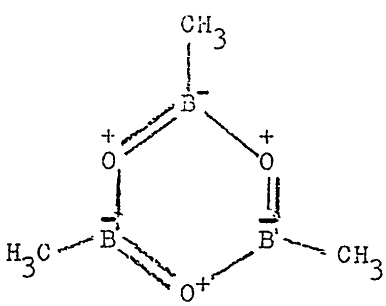
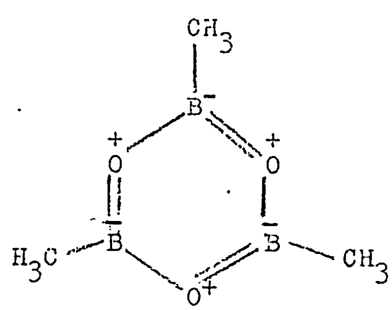
with the ordinary B — N bond (1.58 Å). The $B_3N_3H_6$ molecule represents a regular hexagon conforming with the valence states $\overset{+}{N}$ and $\overset{-}{B}$ (sp^2-hybridization, normal valence angle 120°).

A somewhat different structure is shown for $B_3O_3(CH_3)_3$:



The B_3O_3 is also flat, but the angle B O B ~ 110°, and O B O ~ 130°. This molecule has other possible structures:





But they are probably represented to a lesser degree than structures $\overset{+}{N}$ in $B_3N_3H_6$.

Further, oxygen in ground state and as trivalent positive ion, has only p-electrons as valence electrons for which the valence angle 120° is quite undesirable. The following table shows charges and the number of homeopolar valencies for boron and carbon:

B	C	
4⁻	4	
3	3⁺	3⁻
2⁺	2	
	1⁻	1⁺

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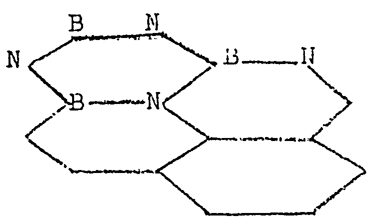
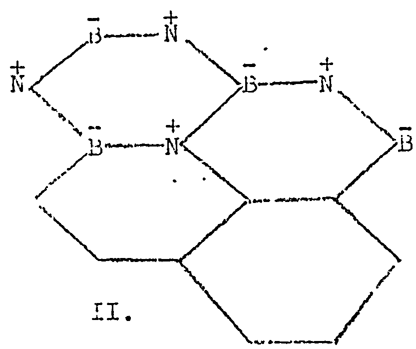
Chemical Bonds In Crystals.

Boron nitride is similar to graphite. Nets, composed of hexagons, have alternating N and B atoms. Next to the homeopolar structure (I) we also have the ionic structure with tetravalent positive N and tetravalent negative B (II) with delocalized double bonds. The distance B N equals that in inorganic benzene (1.45 Å).:



I.

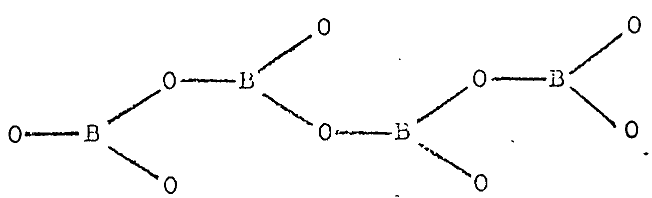


II.

CaB_2O_4 shows anions spreading throughout the lattice. Three atoms of O are situated in the plane around each B atom, forming an almost regular triangle conforming with the direction of three homeopolar boron valencies. Two neighboring B atoms are linked with one common O atom. As a result of such arrangement, we obtain infinite chains of

$$(BO_2)_n^-.$$

Every B retains one active negative oxygen linked with only one boron.



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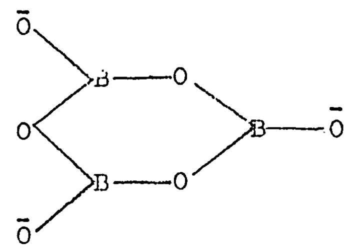
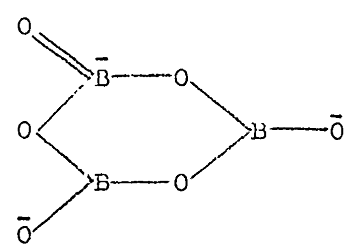
In $K_3B_3O_6$ the BO_3 groups form a ring



A partial representation probably can be found for structures with a negative, tetravalent boron:



Distance of B — O in CaB_2O_4 is 1.36 Å

" " B — $O_{inactive}$ in $K_3B_3O_6$ is 1.38 Å

" " B — O_{active} " " is 1.33 Å

These distances do not coincide with either the sum of ionic radii

(B^{+++} and O^{--}),

or with the sum of covalent radii.

The covalent atomic radii (Pauling) are given as follows [14]:

	single bond	double bond	triple bond
B	0.88 Å	0.76 Å	0.68 Å

Table 2.

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Structure of boron hydrides (boranes). [11].

Boranes occupy a unique position among the chemical compounds, unlike hydrocarbons and silanes, which can be arranged in the frame work of ordinary valency concepts.

Diborane.

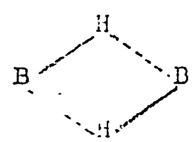
The peculiarity of the simplest borane B_2H_6 lies in its 12 valence electrons which should satisfy 7 bonds (6 B — H bonds and 1 B — B bond). A BH_3 molecule has not been separated. Evidently, BH_3 immediately dimerizes into B_2H_6. Thus, the more stable compound is not BH_3 with normal boron valency, but B_2H_6.

Some researchers try to find a solution in the one-electron bond concept with resonance in various positions. However, the impression is, that the one-electron bond in boranes can be postulated because of lack of another presentation for structures of this class. At the same time, it is suggested that boranes have a configuration of corresponding hydrocarbons. Diborane should have a structure like ethane: H_3BBH_3. Such a configuration must have a one-electron bond.

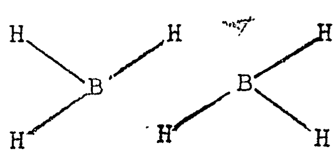
The character of the bonds in B_2H_6 evidently differs from bonds in the isoelectron O_2 molecule, which is paramagnetic, while B_2H_6 is diamagnetic. In order to explain the diamagnetism of boranes by the theory of one-electron bonds, a supplementary hypothesis is necessary.

Nekrasov*, developing the idea of Dilthey, proposed the theory of the "coordinate" structure and opposed the one-electron bond.

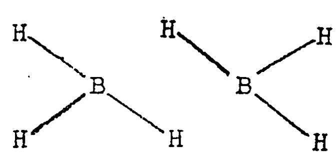
According to Nekrasov, all B atoms are trivalent and only simple covalent bonds and "complex" bonds of the type:



take part in the formation of the molecular structures. In his opinion, the stability of B_2H_6 depends on the presence of the following structures:



I.



II.

*Nekrasov, Zhur.ob.khim., 10, 1021, 1156, (1940).

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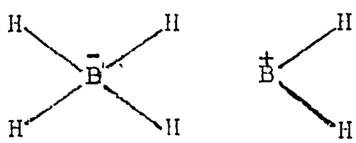
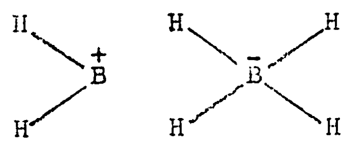
Quantum-mechanical calculations indicate that for purely homeopolar bonds, the resonance energy does not compensate the repulsion of non-bound electrons. If such resonance could stabilize the system, then the molecules H_4, N_2H_6, would exist.

Let us assume that it is possible to demonstrate borane structures without resorting to the one-electron bond, and taking into consideration possible valence states of boron, that is the tetravalent negative, and bivalent positive borons. The presence of two ionic valence states of boron admits the supposition that the B_2H_6 molecule contains one negative, and one positive B atom, the first being linked with four, and the second with two H atoms (III and IV):



III.



IV.

Due to the equivalence of both B atoms, the III structure does not appear to be unique. There exists a valence scheme with reversed distribution of charges (IV), and structural resonance occurs in the real molecule. Energies of both valence schemes III and IV, are equal, resulting in equal participation in the summary state of the system, whereby resonance is at optimum, and the energy gain at maximum. The resonance energy stabilizes the B_2H_6 molecule.

Diborane appears to realize the B — B bond, although it seems to lack a pair of electrons. The bond in this case is formed by the passage of two electrons from one atom to another, similarly to the resonance of two ionic states,

$$\text{e.g., } \overset{+}{H}, \overset{-}{H} \text{ and } \overset{-}{H}, \overset{+}{H};$$

The difference between borane ionic structures and ordinary molecules lies in the fact, that the two electrons at a B atom do not compensate their spins with each other, but with electrons at the H atoms (with the formation of B — H bonds).

The fact, that the BH_3 molecule does not exist, leads us to the conclusion that the bond energy of B — H in the BH_3 is small. This results from the transition of boron from the normal state $1s^22s^22p$ to trivalent $1s^22s2p^2$ requiring energy. The ionic state

$$\overset{+}{H}, \overset{-}{BH_2}$$

is hardly probable, and therefore, cannot contribute to bond strengthening. The B_2H_6 molecule is stabilized by the resonance of two states, III and IV, giving great energy gain, approximately equal to the B — B bond energy. It should be assumed that the resonance energy compensates for the loss involved in the formation of the ionic structure, resulting in greater stability for B_2H_6 than for the two BH_3.

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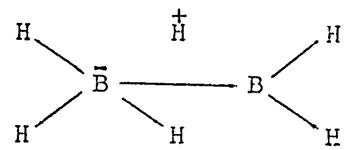
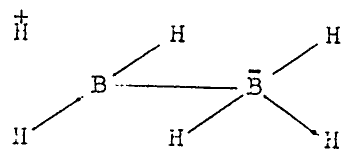
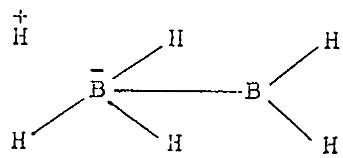
Structures III and IV are not the only ones. The existence of other structures with normal valencies (without the use of one-electron bonds) and the same configuration of nuclei, is possible. Thus, it is possible that the B_2H_6 molecule possesses ionic structures with the charge at the H atom (in spite of structures relating to resonance with ionic B — H bond):



V.
four structures



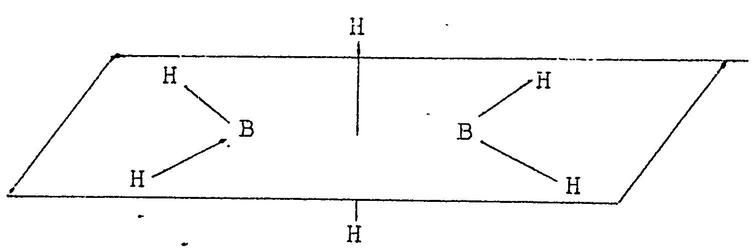
VI.
four structures



VII.
four structures.

Of course, structures V to VII are far less convenient than the basic III and IV. Interchanging all of the above mentioned structures, predominantly III and IV, can condition the stability of boranes without the introduction of hypothetical one-electron bonds.

It is assumed that the atom distribution in a diborane molecule is as follows: two boron atoms and four hydrogen atoms are situated in one plane, and the other two H atoms are placed at equal distances from the plane along the normal to the plane, passing through the center of the B — B line.



This model represents two irregular tetrahedrons with a common edge. In this way, two models were proposed for B_2H_6: the ethane type (two tetrahedrons with a common vertex), and the model shown above. Values of these models need experimental verification. Using electron diffraction, Bauer indicated that the intensity curves calculated for the "ethane" model agree with the experimental curve.

Syrkin and Dyatkina [11] calculated the intensity curve for the second model and came to the conclusion that it agreed with the experimental data to the same degree that Bauer's curve did for the "ethane" model. Thus, the electronographic analysis did not lead to a clear selection of one or the other model.

The calculation of Syrkin and Dyatkina [11] gives the following values for diborane-molecular distances and angles:

$$B - B = 1.80 \pm 0.04 \ \text{Å}$$
$$B - H_{extern.} = 1.23 \pm 0.03 \ \text{Å}$$
$$B - H_{intern.} = 1.33 \pm 0.03 \ \text{Å}$$
$$H\,B\,H_{extern.} = 125^\circ \pm 8^\circ$$
$$H\,B\,H_{intern.} = 95^\circ \pm 5^\circ$$

The distance $B - H_{extern.}$ in B_2H_6 coincides with the distance in the BH molecule (1.216 Å) so there is no need for introducing a particular type of bond in this case. The distance $B - H_{intern.}$ is greater than $B - H_{extern.}$ as this bond is partly weakened. X-ray study of crystal B_2H_6 permits the determination of the B positions, but not of H positions. Consequently, these experimental data do not lead to the justification of this or another model.

Nekrasov [8] presents the following data for the molecular structure of diborane:

Table 3.

	B — B distance	B — H extern. dist.	B — H intern. dist.	H B H extern	H B H intern	d(HH)
B_2H_6	1.79 Å	1.18 Å	1.37 Å	122.5°	98°	2.07Å

The geometrical presentation consists of two regular tetrahedra formed by hydrogen nuclei with common axis, d(HH) = 2.07 Å, and boron nuclei shifted by

$$0.16 \ \text{Å}$$

outwards from the tetrahedral centers.

Syrkin and Dyatkina [11] are using the "ethane" model for the distribution of hydrogen atoms. Such distribution of hydrogen atoms is arbitrary, since it is not verified experimentally.

Chemical properties also indicate that the four H atoms in B_2H_6 differ from the remaining two. It is known that methylation of diborane gives only mono- , di- , tri- , and tetramethyl substituted derivatives. Penta and hexa derivatives were not obtained. Instead of $B_2(CH_3)_6$ we get $2B(CH_3)_3$. On the other hand, $BH(CH_3)$ is known only as a dimer. It is essential to note, that not even a single methyl diborane derivative was obtained, which would have three methyl groups at one B atom. These facts, according to Schlesinger and Burg, lead to two conclusions:

1) in diborane, four hydrogens are linked in a different way than the other two;

2) formation of B — B bonds requires the presence of hydrogen atoms.

Structural data for B_2H_6 given by Ormont, B. F. [9]:

Hexagonal molecular lattice...... H^M or R^M (?)

Coordination..................... 6 (?)

Type .... H^M_6 — SB D41 (ethane)

$H_{c.n.}$ .... = 1B

$B_{c.n.}$ .... = (3 + 3)H

	a	c	c/a	d_{B-B}	OM
B_2H_6	4.54	8.09	1.91	1.82	77.5

Table 4.

Other boranes.

A general theory of borane structure was developed only recently [8] (B. V. Nekrasov, 1940). It is based on the concept of combining valence-saturated structures by means of hydrogen bonds. Taking into consideration trivalent B, its coordination numbers 4 and 3, and also the existence of only simple covalent and hydrogen bonds, the theory determines possible borane type structures, and reveals their characteristic isomerism. According to the theory, composition of all volatile boranes has the general formula:

$$B_nH_{n+2x} \quad \text{where} \quad n \geq 2 \quad \text{and} \quad x = 2, 3, 4 \ldots..$$

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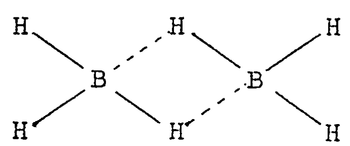
They represent a number of simplest structural elements which together form the molecule of the given borane. Results of the direct determination of spatial borane structures agree with formulas B_2H_6 and B_4H_{10}. Structure of B_5H_{11} ought to be linear ($BH_3 + B_3H_5 + BH_3$) and for B_5H_9, B_6H_{10}, and $B_{10}H_{14}$ the theory foresees the possible existence of several isomeric cyclic structures.

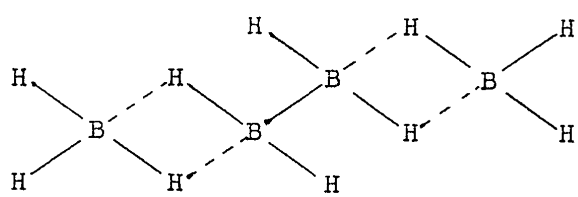
The presence of hydrogen bonds in volatile boranes (with symmetrical distribution of all four nuclei) has been verified by experimental data, and appears to be beyond doubt. Still, no theoretical explanation has been presented for the generation of such bonds. Thus, this problem is of great importance, since "facts unexplained by existing theories are the most precious in science because their solution chiefly will promote its development" (A. M. Butlerov). It is possible that the formation of H bonds occurs in the given case with the participation of inner electrons (i.e., of the K level) of the B atom.

Because of the existence of three external electrons at the B atom, it was expected that B would be not more than trivalent. This should be verified by compounds such as: BH_3 , B_2H_4 , B_3H_5 , etc., but such boranes are not known.

The molecules of volatile boranes should be considered as a result of combining the above mentioned valence-saturated structures by means of H bonds. Thus, we obtain for B_2H_6 and B_4H_{10}:



$BH_3 + BH_3$



$BH_3 + B_2H_4 + BH_3$

The preceeding considerations of Syrkin and Dyatkina [11] on diborane permit certain assumptions concerning structures of other known boranes. It is understood that all these compounds reveal superposition of structures with positive bivalent, and negative tetravalent boron atoms. At the same time, there exists also the ordinary trivalent boron in molecules. The following borane structures are given with greatest weights. It will be shown that these structures do not exhaust all the possibilities.

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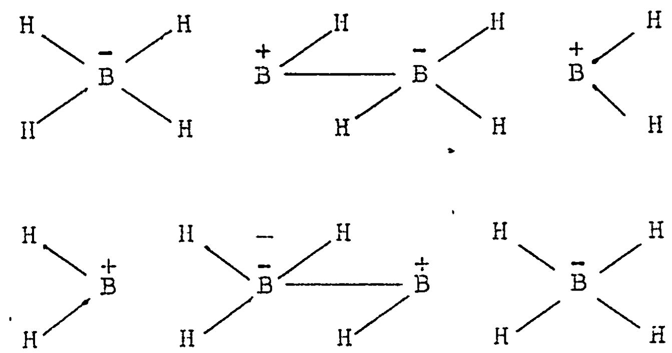
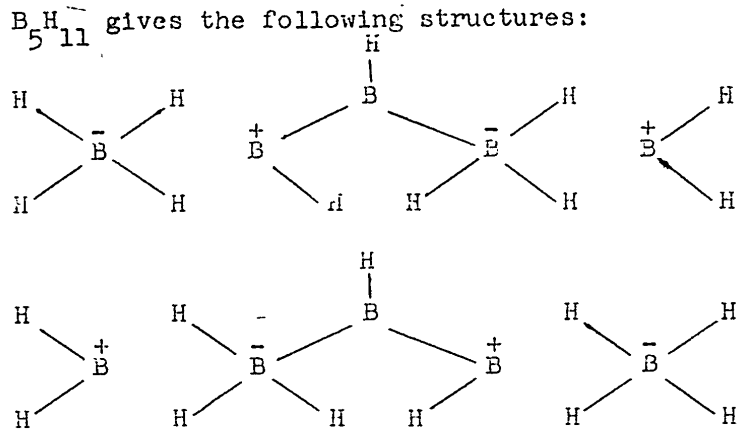
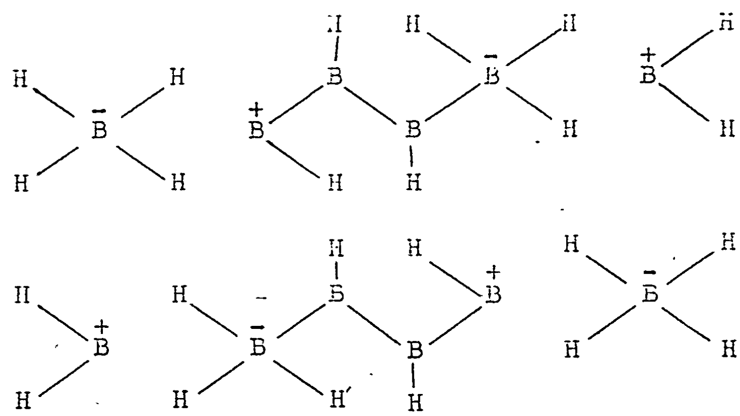
The molecule B_4H_{10} reveals resonance of the following states:



The compound $B_5H_{11}^-$ gives the following structures:



In B_6H_{12} the following resonance of structures takes place:



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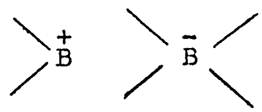
All these molecules have B atoms at their ends, with linkages of this type:



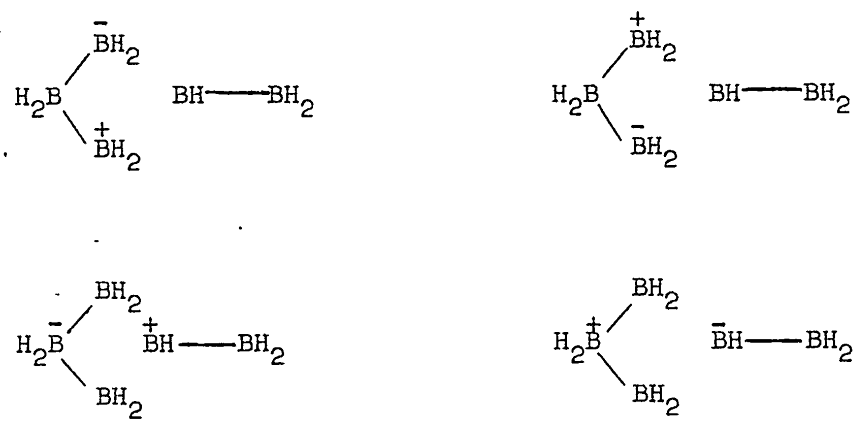
It is easy to see that the general formula of these compounds is

$$B_2H_8\ (BH)_n \quad \text{or} \quad B_{n+2}H_{n+8}\,, \text{ where } n \geq 2.$$

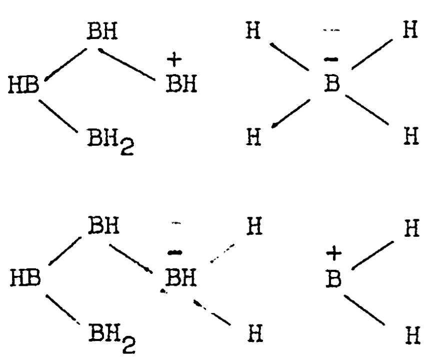
Other compounds on the same principle are also possible, e.g., B_5H_9, B_6H_{10}, and $B_{10}H_{14}$.

The molecule of B_5H_9 reveals different types of structure:

Type A

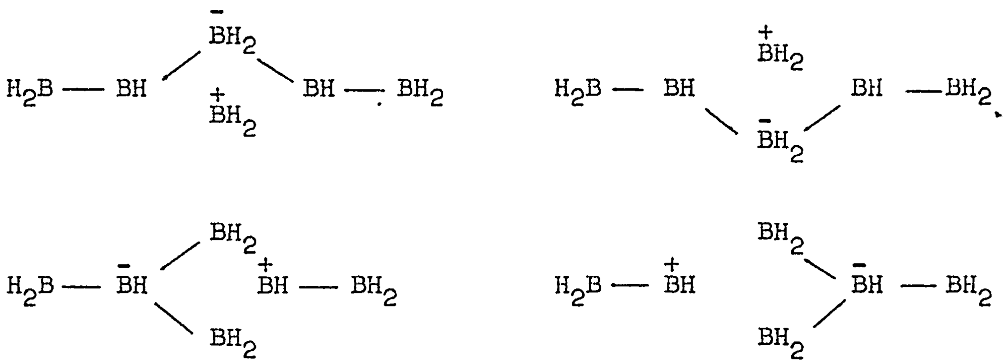


Type B

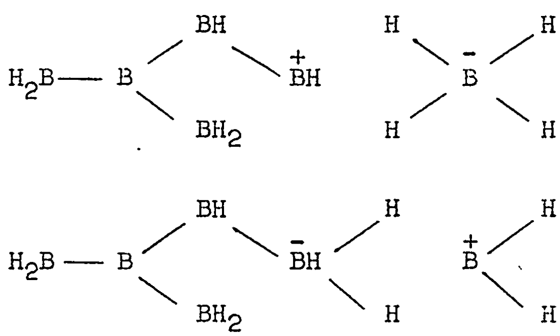


Models of configurations for B_6H_{10} , based on accepted structural principals:

Type A

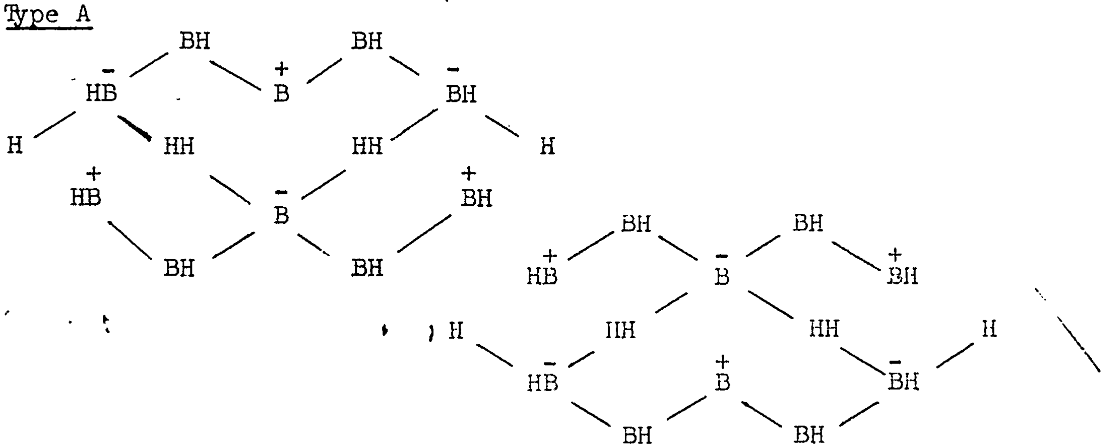


Type B

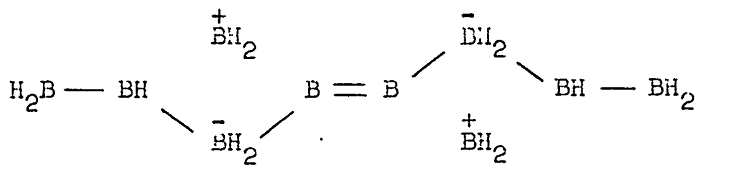


The molecule of $B_{10}H_{14}$ discloses various possible cyclic forms:

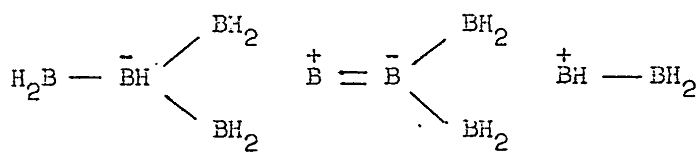
Type A



Type B

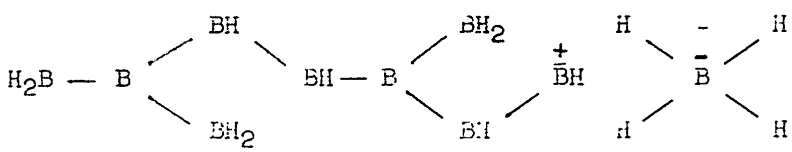


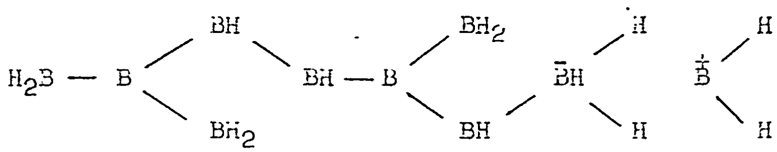
four structures



two structures

Type C



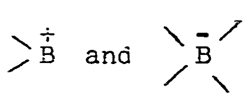


It is obvious that the general formula for these compounds is:

$$B_nH_{n+1} \cdot BH_4 \quad \text{or} \quad B_{n+1}H_{n+5} \quad (B_2H_6,\ B_5H_9,\ B_6H_{10},\ B_{10}H_{14}).$$

The essential fact is that in all the mentioned structures there is no necessity for one-electron bonds, the number of which is usually determined post factum from the given formula.

According to the developed concepts, all boranes have configurations based on one principle. They contain a certain amount of ordinary trivalent boron atoms together with some in the state of



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Studies of the physical and chemical properties of boranes lead to the conclusion that boranes:

$$B_5H_9,\ B_6H_{10},\ B_{10}H_{14},$$

are more stable than

$$B_4H_{10},\ B_5H_{11},\ B_6H_{12}.$$

The quoted formulas indicate that the first group possess more resonance structures and more B — B bonds.

The existence of B_3H_8 should seem possible from the point of view of the one-electron bond theory. In any case, if this compound were to be detected, the supporters of the one-electron bond concept would have no difficulty in formulating its structure. Seeking hydrocarbon analogs, it would be recognized as propane like, exactly the way B_2H_6 is considered ethane like. It is interesting to note that n ot even one borane is known with an odd number of electrons

$$B_3H_8,\ B_5H_{12}\ldots\ldots \text{ etc.}).$$

It is impossible to formulate structures of such compounds in the framework of the above quoted concepts. The fact, that in spite of the great number of synthesized boranes such compounds were not detected, evidently is not accidental, and can be regarded as one of the proofs for the validity of the proposed principle of borane structure.

It is interesting that diborane decomposes whenever there is a possibility of forming compounds with tetravalent negative boron:

$$B_2H_6 + 2CO \longrightarrow 2\overset{-}{B}H - \overset{+}{CO},$$

$$B_2H_6 + 2N(CH_3)_3 \longrightarrow 2\overset{-}{B}H_3 - \overset{+}{N}(CH_3)_2.$$

The product of the interaction of B_2H_6 with ammonia is represented by the formula $B_2H_4(NH_4)_2$ as if we had a bivalent B_2H_4 ion. But in fact, this molecule is better expressed by the structure:

$$\left|\ \overset{-}{B}H_3 - \overset{+}{N}H_2 - \overset{-}{B}H_3\ \right|\ \overset{+}{N}H_4,$$

which agrees with the behavior of this substance in liquid ammonia. It is also known that there is no B — B bond in $B_3N_3H_6$ and B_2NH_7, but the B — N — B bond.

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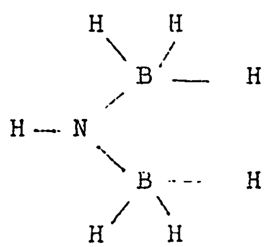
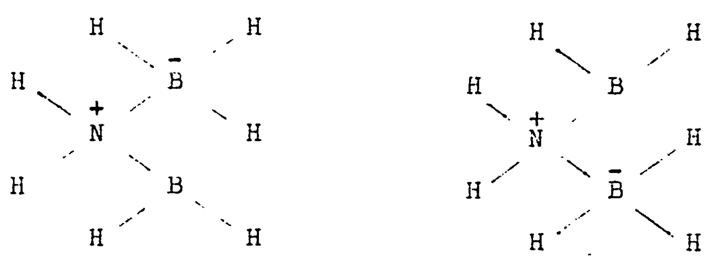
Two models are considered for the B_2NH_7 molecule:

1) dimethylamine like

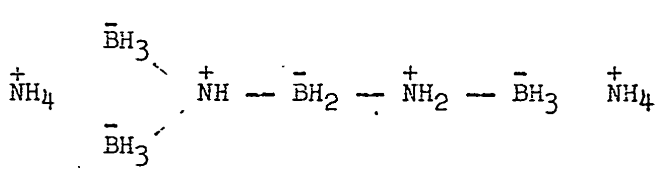


2) with resonance of two structures



The electronographic analysis does not permit a definite choice. On the other hand, chemical data largely agree with the second model.

The product of the addition of four NH_3 molecules to B_4H_{10} is represented by the formula: $(B_4H_6)(NH_4)_4$, which is hardly probable, as the B_4H_6 ion with four negative charges ought to be very unstable. The following structure is regarded as more probable:



Alkali metals also add to boranes forming compounds of higher stability than the original boranes. $B_2H_6K_2$ probably has the following structural formula:

$$\overset{+}{K} \quad \overset{-}{B}H_3 — \overset{-}{B}H_3 \quad \overset{+}{K}.$$

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It is interesting to note that whereas B H does not exist, the compound $B_4H_{10}K_2$ is known, and may have the following formula:

$$\overset{+}{K}\,\overset{-}{B}H_3 — BH — BH — \overset{-}{B}H_3\,\overset{+}{K}.$$

The compound LiBH appears to be noticeably polar and has the structure of

$$\overset{+}{Li}\quad \overset{-}{B}H_4.$$

The structure Li — $\overset{-}{B}H_3\,\overset{+}{H}$ is less probable. This is apparently the reason why $LiBH_4$ does not react with $N(CH_3)_3$. On the contrary, the structure

$$\overset{-}{B}H_4\quad \overset{++}{Be}\quad \overset{-}{B}H_4 \quad \text{for} \quad Be(BH_4)_2$$

is hardly probable. Of considerable weight are the structures:

$$\overset{+}{H}\,\overset{-}{B}H_3 — Be — \overset{-}{B}H_3\,\overset{+}{H}$$

16 structures

$$\overset{+}{H}\,\overset{-}{B}H_3 — \overset{+}{Be}\quad \overset{-}{B}H_4$$

8 structures

Hydrogen in this compound is mostly positive, what leads to the possibility of addition products $Be(BH_4)_2\ N(CH_3)_3$ with structure:

$$\overset{-}{B}H_4\quad \overset{+}{Be} — \overset{-}{B}H_3\quad \overset{+}{N}H(CH_3)_3,$$

and probably to a lesser degree

$$\overset{+}{H}\,\overset{-}{B}H_3 — Be — \overset{-}{B}H_3\,\overset{+}{N}H(CH_3)_3.$$

In case of $Al(BH_4)_3$ evidently the prevalent structures are:

$$\begin{array}{lll} \overset{+}{H}\,\overset{-}{B}H_3 & & \\ & \searrow \ Al — \overset{-}{B}H_3\,\overset{+}{H} & \\ \overset{+}{H}\,\overset{-}{B}H_3 & \nearrow & \end{array} \qquad\qquad \begin{array}{lll} \overset{+}{H}\,\overset{-}{B}H_3 & & \\ & \searrow \ \overset{+}{Al} \quad \overset{-}{B}H_4 & \\ \overset{+}{H}\,\overset{-}{B}H_3 & \nearrow & \end{array}$$

64 structures — 48 structures

This explains the high reactivity with $N(CH_3)_3$.

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Thus, compounds of this class can easily be described in terms of ordinary valence schemes without one-electron bonds. In any case, the

$\overline{B}H_4$

group undoubtedly enters all quoted molecules as a structural unit.

A certain similarity to boranes is evident in compounds of boron analogs. There is evidence that a halogen hydride also forms a dimer, Hal_2H_6.

Al_2Cl_6, Al_2Br_6, Al_2I_6, $Al_2(CH_3)_4Cl_2$, and $Al_2(CH_3)_4Br_2$ have the atomic configuration as in the model for B_2H_6. There are various opinions on $Al_2(CH_3)_6$. Electronographs agree better with the ethane-like configuration, and the Raman spectra agree with the second model. .

Structural data for $B_{10}H_{14}$ given by Ormont, B. F. [9]:

Rhombic lattice .... OR

Coordination .... (?)

Type .... (?)

Space group .... D_{2h}^{21} — Cmma

Z 8

Table 5.

	a	b	c	a a : b : c
$B_{10}H_{14}$	14.46	20.85	5.69	0.69 : 1.00 : 0.27

Physical properties of boranes. [12]

Boranes are known as gaseous, liquid, and solid substances. Some of them are not stable in air, others are relatively stable, but in comparison with hydrocarbons, they are considerably more active chemically. Boranes are acidic, therefore they form salt-like compounds with ammonia. These compounds produce a series of other boron-hydrogen-nitrogen compounds when heated. Among these compounds, borazole is the most interesting. It is very much like benzene in its configuration and physical properties.

The best known so far [8], are six boranes: Table 6.

	B_2H_6	B_4H_{10}	B_5H_{11}	B_5H_9	B_6H_{10}	$B_{10}H_{14}$	
melt. p.	-166	-120	-123	-47	-65	+99	
boil. p.	-93	+18	63	48	110	213	

All these boranes are colorless, are toxic, and have a repulsive odor. Even slight amounts of their vapors cause bad reactions if inhaled.

Their pure gases, free of impurities, do not ignite spontaneously in air. Under normal conditions,

$$B_5H_{11} , B_5H_9 , \text{ and } B_6H_{10}$$

are liquid. Some solid boranes are known, with a lower H content, typical coloration, mostly shades of yellow, and are soluble in CS_2. Those with the lowest H content are of a brown color, similar to that of free boron.

Properties of boranes and of their derivatives [12] Table 7.

Compound	formula	m.p. °C	b.p. °C	sp.gr. (°C)	vapor pressure mm (°C)	properties
diborane	B_2H_6	-165.5	-92.5	0.447 (-122)	225 (-111.9)	Detonates in presence of humidity, ignites in air, thermally unstable
Tetraborane	B_4H_{10}	-120	18	0.56 (-35)	388 (0)	Ditto

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Properties of boranes and of their derivatives [12] (Continued)

Compound	formula	m.p. °C	b.p. °C	sp.gr. (°C)	vapor pressure mm (°C)	properties
Pentaborane stable	B_5H_9	-46.6	48.6 151/131 mm	0.630 (16)	66 (10)	Does not ignite in air at 10-20°. Very slow hydrolysis.
Pentaborane unstable	B_5H_{11}	-123	63	-	53 (0)	Spontaneous ignition in air, decomposes at room temperature.
Hexaborane	B_6H_{10}	-65.1	0/7.2 mm	0.69 (0)	-	Does not ignite in air, slow decomposition, slow hydrolysis.
Decaborane	$B_{10}H_{14}$	99.7	213 156/1624 mm	0.92 (99)	19 (100)	Does not ignite, does not decompose. Slow hydrolysis.
Borazole	$B_3N_3H_6$	- 58	55	0.8519	-	Chemically stable. Soluble in water without reaction, hydrolyzes when heated.
Diborine amide	$B_2H_5NH_2$	- 66.4	76	-	-	Decomposes slowly.
Aluminum borohydride	$Al(BH_4)_3$	- 65.4	44.5	0.5588 0(13.8)	119.5 (10)	Reacts vigorously with water and oxygen.
Lithium borohydride	$LiBH_4$	273 with decomp.	-	-	-	Does not react with oxygen when dry.
Beryllium borohydride	$Be(BH_4)_2$	31	91.3	-	5.12	Reacts vigorously with water and oxygen from air.
Sodium borohydride	$NaBH_4$	400				Solids, decompose when heated, partly sublimate in vacuum.
Salt of boranes	$K_2B_2H_6$ CaB_2H_6 $Na_2B_4H_{10}$					

The vapor pressure of diborane " p " in mm Hg, the surface tension "γ" in dynes per cm, and viscosity "η" in millipoise, can be computed from the following equations:

$$\log p = 7.185 - 782.8/T ;$$
$$\gamma = (65.7 - 0.277T)d^{2/3} ;$$
$$\eta = 36.86 \cdot 10^{-5} d^{1/3} e^{651.8d/T} ,$$

where T = temperature

d = density

e = base of natural logarithms.

The critical temperature and critical pressure for diborane are: 16.7 and 40.6 atm respectively.

Physical properties of diborane B_2H_6 (12). Table 8.

T, °K	Vapor pressure, mm Hg		T, °K	Liquid density g/cm³	T, °K	Density of gas g/cm³
	exp.	calc.				
243.1	8890	9200	243.6	0.333	246.2	0.0382
249.9	10800	11300	249.9	0.316	251.3	0.0393
256.1	13400	13400	255.9	0.307	255.3	0.0470
268.1	19000	18400	268.1	0.285	260.8	0.0492
275.8	21700	22200	275.9	0.259	265.8	0.0541
277.3	22400	23000	277.8	0.253	270.7	0.0588
277.8	22700	23200	-	-	274.0	0.0625
284.0	26300	26800	284.1	0.231	285.2	0.0927
287.1	28100	28700	287.1	0.213	288.2	0.1100
288.9	30200	29800	288.4	0.154		

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The second virial coefficient for diborane [15]

Table 9.

$T\ ^{o}K$	B in cm^3/mol
275.16	- 227

The only value of B for diborane was computed by Carr from P -V -T data (E.M. Carr, J.T. Clarke, H.L. Johnston, J.Am. Chem. Soc. 1949, 71, 740).

A suggestion was made recently, for a general equation for the computation of boiling points of hydrocarbons and silanes:

$$T_k = a \ln (n + b) + k$$

where $T =$ boiling point in ^{o}K

$n =$ number of central atoms

$a, b, k =$ constants.

The equation takes the following form for silanes:

$$T = 395.8 \ln (n + 3.5) - 416.31 .$$

Data computed for disilane Si_2H_6, trisilane Si_3H_8, and tetrasilane Si_4H_{10}, differ from experimental data only by fractions of a degree.

This equation was tested for boranes, but did not give satisfactory results due to the complex structure of such compounds.

Density, surface tension, and viscosity of pentaborane can be computed from the following equations:

$$d = 0.8674 - 0.00082T ,$$

$$\gamma = (71.1 - 0.1437T)\, d^{2/3} ,$$

$$\eta = 41.15 \cdot 10^{-5}\, d^{1/3}\, e^{1024d/T}$$

Physical properties of pentaborane B_5H_9 [12].

Table 10.

Temp. °K	density g/cm³	Temp. °K	viscosity, millipoise	Temp. °K	Surface tension dyne/cm
226.0	0.681	232.2	7.82	233.9	28.9
227.0	0.681	245.0	5.29	245.1	27.4
235.2	0.675	246.5	5.64	249.0	27.0
235.4	0.675	253.2	5.14	264.7	24.8
246.1	0.666	258.4	4.78	286.0	22.0
253.0	0.660	264.1	4.45	303.3	20.0
263.2	0.652	269.5	4.17	-	-
277.6	0.642	274.1	3.94	-	-
283.5	0.635	279.6	3.68	-	-
289.3	0.630	286.4	3.42	-	-

The thermochemical properties of boranes and borohydrides are not sufficiently covered in literature. Data published by various authors are often divergent.

In 1946, aluminum borohydride was characterized by the heat of formation equal 7.2 kcal/mole, and diborane B_2H_6 by 29.5 kcal/mole. In 1948, the heat of formation for B_2H_6 was given as -6.63 kcal/mole based on the heat effect in the hydrogenation of boron:

$$2B(\text{solid, amorphous}) + 3H_2(\text{gas}) \longrightarrow B_2H_6(\text{gas}) - 6.63(0.52)\ \text{kcal/mole.}$$

This reaction is endothermic, which is quite probable, since the pyrolysis of diborane occurs with heat generation.

The heat of combustion of diborane according to:

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O + 508.5\ \text{kcal}$$

is determined from the heat of formation of diborane, water, and boric anhydride. But there are different values for the heat of formation of B_2O_3.

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Heat of formation of B_2O_3 [12]

Table 11.

Author	year	heat of formation kcal/mole
Berthelot	1878	279.9
Roth	1937	349
Roth	1946	345
Tod, Müller	1946	335
Prosen, et al.	1948	303
Eggerlus, Monroe	1949	281.1
Johnston, et. al.	1951	302
E.V.Britske, A.F. Kapustinskiy	1949	349

Such discrepencies are explained by experimental difficulties. The heat of evaporation for B_2O_3 is given as 65.6 kcal/mole and 77.6 kcal/mole.

The maximum and minimum values for the heat of combustion of diborane B_2H_6, when the heat of formation for B_2O_3 equals 335 kcal/mole, and the heat of evapration is 65.6 kcal/mole, are equal respectively:

$$Q_{max} = 18.4 \text{ kcal/g}$$

$$Q_{min} = 16.0 \text{ kcal/g} ,$$

and the minimum heat of combustion for the mixture $B_2H_6 + 3O_2$ equals 3.58 kcal/g.

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In discussing the thermodynamic properties of substances, Vol'kenshteyn [14] gives the following value for the inner rotation energy of diborane:

Table 12.

	bond	barrier (cal/mole
B_2H_6	B — B	4000 — 6000

Although stable pentaborane B_2H_6 does not ignite in air at room temperature, yet its vapors do react with pure oxygen, and with detonation.

Conditions for the detonation of the B_5H_9 — O_2 mixture in a spherical quartz container, at room temperature.

Table 13 [12].

	Diameter of the vessel: 3.7 cm								
Vapor pressure of B_5H_9, mm	0.77	0.83	4.45	4.36	1.00	1.74	1.57		
Pressure of O_2, mm	2.9	2.8	1.9	2.1	2.7	2.2	2.4		
Results*	det.	no	no	det.	no	no	no		
	Diameter of the vessel: 6.62 cm								
Vapor pressure of B_5H_9, mm	1.03	1.01	1.98	1.94	2.98	3.01	4.02	4.08	
Pressure of O_2, mm	1.5	1.66	1.32	1.33	1.18	1.25	1.13	1.19	
Results *	no	det.	no	det.	no	det.	no	det.	

* Det. = detonation occured, no = detonation did not occur

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The lower-limit concentration depends on the pressure of the B_5H_9 — O_2 mixture, volume of the vessel, and also its pressure.

Detonation of the B_5H_9 — O_2 mixture at room temperature was observed at a total pressure in the system of 3 - 6 mm, but the initiation of detonation depended on the composition of the mixture and the volume of the vessel, as shown in the previous table.

Some thermodynamic functions for decaborane $B_{10}H_{14}$ are given in the following table:

Table 14 [12].

Temp. °K	C_p cal/deg.mole	S cal/deg.	$H^o - H^o_o$ cal/mole	$(H^o - H^o_o)/T$	$(F^o - H^o_o)/T$
14	0.810	0.270	2.835	0.203	0.067
25	3.350	1.352	24.714	0.989	0.363
50	8.135	5.381	176.86	3.537	2.207
75	11.135	9.300	421.08	5.614	3.686
100	13.325	12.799	726.47	7.265	5.534
125	16.30	16.074	1094.8	8.758	7.316
150	20.03	19.365	1547.5	10.317	9.048
175	24.62	22.790	2104.3	12.025	10.765
200	29.82	26.414	2784.3	13.922	12.423
250	41.02	34.254	4551.3	18.205	16.049
275	47.13	38.448	5652.7	20.555	17.893
298.16	52.42	42.475	6806.9	22.830	19.645
300	52.78	42.798	6903.7	23.012	19.786

The molecular weight of decaborane equals 122.31, consequently its heat capacity by weight at 25° equals 0.429 cal/deg.g.

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Borazole $B_3N_3H_6$, the inorganic analog of benzene, requires special attention. It is a colorless, transparent, mobile liquid, with an odor characteristic of aromatic compounds. It easily dissolves fats.

The density of borazole, in the temperature range of -40 to +10° can be computed from the equation: $d = 0.8613 - 0.00097\ T$. The vapor pressure of borazole at -33° is 11.6 mm

at -33°	is 11.6 mm	at 40.2°	is 456.2 mm
" -20°	" 29 mm	" 51.2°	" 670.9 mm.
" 0°	" 85.1 mm		
" 20°	"210 mm		

This can be expressed by the equations:

$\log p = -1565/T + 7.6616$ ....from - 15 to + 20°

$\log p = -1538/T + 7.5668$ ....from + 20 to + 50°,

where T is temperature in $^\circ$K.

The surface tension which is:

31.09 dyne/cm .... at 58.0

24.24 " .... " 3.0

can be determined from the equation: $\gamma = 24.42 - 0.115\ T$.

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Comparison of the physical properties of borazole and benzene [12].

Table 15.

Properties	$B_3N_3H_6$	C_6H_6
Molecular weight	80	78
M.p., °K	215	279
B.p., °K	328	353
Critical temperature, °K	525	516
Density of liquid at b.p.	0.808	0.81
Heat of vapor formation, kcal/mole	7.0	7.4
Surface tension at b.p., dyne/cm	31.1	31.0
Parachor	208	206
Trouton constant	21.4	21.1
Interatomic distance in ring, A	1.44	1.39

Properties of borazole halo derivatives [12].

Table 16.

Compound	m.p., °C	b.p., °C	Trouton constant
$B_3N_3H_5Cl$	-34.6	109.5	22
$B_3N_3H_5Br$	-34.8	122.3	25
$B_3N_3H_4Cl$	—	151.9	21
$B_3N_3H_4Br$	—	167.1	29

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The thermal dependence of the vapor pressure of monochloroborazole $B_3N_3H_5Cl$ is:

Table 17 [12].

$T,\ ^{\circ}K$	273.2	282.7	298.7	320.2
Vapor pressure, mm	8.8	14.9	33.3	86.7

Chemical properties of boranes [8] [12].

In dealing with the chemical properties of boranes, it is important to note that their B atoms do not appear to be completely shielded. As a result of the addition of various particles from the medium, two trends of the elementary process are possible: cleavage of the H bonds, or migration of the protons. Occurrence of one or the other depends on the character of the addition particles. And so, in the reaction of boranes with ammonia, the first variation takes place, and in the reaction with hydrogen halides, the second.

The reaction of boranes with ammonia gives white salts (addition products) in which the number of added NH_3 molecules equal the number of B atoms with hydrogen bonds. Cleavage of these bonds is an essential part of the primary reaction:

$$NH_3 + B_2H_6 + NH_3 = 2\ H_3BNH_3$$

then follows the secondary reaction:

$$2\ H_3BNH_3 = NH_4\ [BH_3NH_2BH_3].$$

The substitution of ammonia with trimethylamine or CO stops the process in the first stage giving respectively: $H_3BN(CH_3)_3$ for which the m.p. is 94° and b.p. 171°, and H_3BCO, b.p. -64°.

Both these compounds have donor-acceptor bonds: $d(BN) = 1.62\ \mathring{A}$, $d(BC) = 1.57\ \mathring{A}$, where the B atom acts as acceptor.

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The stability of the products of ammonia addition generally decreases with the growth of the borane series, $B_2H_6 \longrightarrow B_{10}H_{14}$.

Thus, $B_2H_6 \cdot 2NH_3$ decomposes in vacuum only at $+90^\circ$, while $B_{10}H_{14} \cdot 6\,NH_3$ completely loses ammonia under ordinary conditions.

Many organic solvents dissolve boranes completely. But in water, boranes hydrolyze easily, better than silanes, liberating hydrogen:

$$B_2H_6 + 6\,H_2O = 2\,B(OH)_3 + 6\,H_2$$

The rate of this reaction diminishes with the increase of the B order in boranes, from $B_2 \longrightarrow B_{10}$.

Like silanes, boranes do not react with concentrated sulfuric acid. With strong alkalies, they behave unlike silanes: a bar of KOH placed in B_2H_6 becomes coated with crystalline potassium hypoborate:

$$B_2H_6 + 2\,KOH = K_2B_2H_6O_2 + H_2.$$

This is true for other gaseous boranes, and strong solutions of strong alkalies. Apparently, the interaction of liquid boranes with alkali solutions does not occur in the same way as for gaseous boranes. At first, they dissolve without hydrogen formation. Then, acidification of the solution initiates the decomposition into H_3BO_3 and H_2, which proceeds very slowly, and needs several days for completion. Evidently, alkali solutions of liquid boranes form salts of more stable acids, than solutions of gaseous boranes. It is possible that these salts are identical with salts of various hypoboric acids $H_xB_2O_y$ with varying values for x (2,4,6) and y (2,4) obtained from the reaction of Mg_3B_2 with alkalies. These salts, and also derivatives of $H_2B_4O_6$ obtained at the same time, are colorless, crystalline, and form solutions which are strong reducing agents.

Certain acids of this type are so stable that they can be separated in free state. Heating of $H_4B_2O_4$ and $H_2B_4O_6$ in vacuum gives their anhydrides, boron oxides, with formulas: B_2O_2 and B_4O_5.

Both are colorless and soluble in water.

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Diborane B_2H_6 [12].

Diborane is a colorless gas with good reactivity, soluble in ether and carbon bisulfide, rapidly hydrolyzed in water. In abscence of humidity it does not ignite in air, but in humid air it ignites with detonation. During storage it decomposes very slowly. In pure form, in a sealed glass container, it does not show more than a loss of 10 percent per year. For instance, if the initial content was 99.4 percent of diborane and 0.6 percent of gas, after 6 months of storage at -18°, about 2 percent of diborane decomposed. The sample showed 97.2 percent of diborane, 1.5 percent of tetraborane, and 1.3 percent of gas which does not condense at the boiling point of diborane. At the temperature of ca 100° diborane decomposes into tetraborane, pentaborane, and solids.

Tetraborane B_4H_{10} [6] [12].

Tetraborane is a colorless gas, well soluble in benzene. At room temperature it is liquid, and has a characteristic unpleasant odor. Its vapors cause headache, nausea, and incapacity. It ignites spontaneously in air, whether crude or purified [6]. If small amounts of air are added to a system containing tetraborane, an immediate flash follows, and the walls of the container become coated with a solid, containing boron, evidently the product of incomplete combustion of boranes. It hydrolyzes slowly in water, but rapidly in strong solutions of alkalies.

According to manometric data, crude tetraborane decomposes faster when stored, than tetraborane obtained after fractional distillation. Pure tetraborane can be stored at room temperature for several days, without appreciable decomposition. After prolonged storage, pressure increases, and a sediment, evidently of high molecular weight boranes, is visible on the walls of the vessel. For longer storage, tetraborane should be placed in a cooling mixture (solid carbon dioxide with alcohol).

Tetraborane is exceedingly active, and reacts readily with the sealing greases of apparatus. It should be in contact only with glass or mercury.

Pentaborane B_5H_9 [12].

This pentaborane is called "stable". Prolonged storage of this pentaborane (for several years) at room temperature, revealed only negligible decomposition of B_5H_9 with the formation of hydrogen and solid residue. The slow decomposition of stable pentaborane becomes evident at 150° , and it is rapid at 300° . B_5H_9 does not ignite in air, but a mixture of pentaborane vapors ignites with pure oxygen. Hydrolysis in water occurs very slowly. The hydrolysis at 90° and 72 hours is not complete. Stable pentaborane shows good solubility in hydrocarbons, cyclohexane and benzene.

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Pentaborane B_5H_{11} [12].

This pentaborane is called "unstable", since it decomposes at room temperature into B_2H_6 , B_4H_{10} , and $B_{10}H_{14}$. It ignites spontaneously in air. It appears to be the least stable of all the boranes mentioned. B_5H_{11} is obtained from the thermal decomposition of other boranes.

Hexaborane B_6H_{10} [12].

When stored for a longer time at room temperature, hexaborane decomposes completely. This points to its lesser stability in comparison with diborane. When hexaborane vapors are passed through a tube heated to 300°, the decomposition of B_6H_{10} is not yet complete.

Dissolved in water, it slowly hydrolyzes, and even when heated to 90° for the duration of 16 hours, this hydrolysis is not complete.

Decaborane $B_{10}H_{14}$ [12].

Decaborane is a completely stable, solid substance. As compared with the other boranes, it has the greatest chemical stability. Noticeable decomposition of $B_{10}H_{14}$ occurs only at temperatures above 170°. Decaborane does not react with oxygen in air at room temperature, also not at 60°, but at 100° it ignites spontaneously. It hydrolyzes in water very slowly at room temperature, and rapidly during boiling. It dissolves well in alcohol, ether, and benzene.

Preparation of boranes [12] [8].

Ordinarily, Mg_3B_2 [11] is treated with 8N-solution of H_3PO_4.

Resulting boranes are separated by fractionation (in absence of air).

The early method of treating Mg_3B_2 with HCl gave poor yields, less than 3 percent. Preparation of diborane and borohydrides in larger quantities was possible after the introduction of the method of reacting boron halides with metal hydrides and lithium aluminum hydride in absolute ether:

$$4\ LiH + BF_3 \longrightarrow LiBH_4 + 3\ LiF\ ,$$

$$3\ LiBH_4 + BF_3 \longrightarrow 2\ B_2H_6 + 3\ LiF\ ,$$

$$3\ LiAlH_4 + 4BF_3 \longrightarrow B_2H_6 + 3\ AlF_3 + 3\ LiF\ ;$$

$$4\ LiAlH_4 + 4BF_3 \longrightarrow Al(BH_4)_3 + LiBH_4 + 3\ AlF_3 + 3\ LiF\ ,$$

$$3\ NaBH_4 + 4BF_3 \longrightarrow 2\ B_2H_6 + 3\ NaBF_4\ .$$

Instead of using gaseous BF_3 it was suggested that its liquid ethyl etherate $(C_2H_5)_2O \cdot BF_3$ be substituted. The reaction of LAH with $(C_2H_5)_2O \cdot BF$ takes place in ether, at a temperature of 0 to 35°. The following table gives results of the reaction of 20.78 g $(C_2H_5)_2O \cdot BF_3$ in 80 ml of ether, with a variable amount of LAH solution in 100 ml of ether:

Table 18 [12].

Volume of $LiALH_4$ solution, ml	molar ratio of $LiAlH_4/BF_3$	volume of B_2H_6 obtained, ml
25.0	0.251	272.2
45.0	0.451	751.3
65.0	0.652	931.6
75.0	0.752	1096.2
85.0	0.852	1100.3

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An almost quantitative conversion (yield of ca 90 percent) of BF_3 into B_2H_6 is observed for the following ratio of reagents, close to the theoretical: 4.5 — 5.0 mole BF_3 to 3 moles of $LiAlH_4$.

In case of using $LiBF_4$ as the source of boron fluoride, the reaction runs as follows:

$$3\ LiAlH_4 + 4\ LiBF_4 \longrightarrow 2\ B_2H_6 + 3\ LiF + 3\ AlF_3.$$

The best results are obtained for the theoretical ratio of reagents, and during the heating of the reacting mixture to $\sim 350^{\circ}$. The yield then reaches 45 percent of B_2H_6.

Mikheeva and Fedneva [3] studied the preparation of diborane for the preparation of a product of high purity, and constant yield. A systematic review was made of LiH reductions of the simplest inorganic boron compounds: halides, sulfides, borofluorides of alkaline metals, etc. It was established that all these substances react with LiH explosively, and with the formation of elementary boron.

A diluted ether solution of boron trifluoride reacts with LiH at room temperature, forming diborane after a considerable induction period. But the reaction takes place immediately with the etherate of boron trifluoride (b.p. 126°). The gaseous substance obtained appears to be practically pure diborane without admixtures, except for some ether vapors. This reaction turned out to be erratic, with yields from 20 to 60 percent.

Considering the following reactions:

$$6\ LiH + 2\ BF_3 \xrightarrow{\text{promoter}} B_2H_6 + 6\ LiF \qquad (1)$$

$$6\ LiH + 8\ BF_3 \longrightarrow B_2H_6 + 6\ LiBF_4, \qquad (2)$$

and with an adequate amount of the promoter:

$$6\ LiH + 1.5\ BF_3 \xrightarrow{\text{promoter}} 1.5\ LiBH_4 + 4.5\ LiF,$$

$$1.5\ LiBH_4 + 0.5\ BF_3 \longrightarrow B_2H_6 + 1.5\ LiF,$$

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Mikheeva and Fedneva point out the great complexity of the reaction. The presence of an activator soluble in ether, $LiBH_4$ or $LiBH(OCH_3)_3$, leads to the conversion principally into $LiBH_4$. With the activator absent, the reaction yields B_2H_6 and $LiBF_4$. High pressure and presence of tetrahydrofuran, in which diborane dissolves easily, favor the formation of lithium borohydride. The erratic character of the yield of the reaction is stressed.

The reaction: $3\ LiH + 3\ BF_3 \cdot O(C_2H_5)_2 \longrightarrow 3\ LiBHF_3 + 3\ (C_2H_5)_2O$

$$3\ LiBHF_3 + BF_3 \cdot (C_2H_5)_2O \longrightarrow 1/2\ B_2H_6 + 3\ LiBF_4 + (C_2H_5)_2O,$$

shows that consecutive additions of the etherate react with diminishing vigor, in spite of the presence of lithium hydride in excess.

Mikheeva and Fedneva regard this reaction as difficult and not quantitative, and give preference to the reaction of boron trifluoride with trimethoxyborohydride $NaBH(OCH_3)_3$, which gives a more constant yield of diborane.

The preparation of diborane from the reaction of lithium hydride with the etherate of boron trifluoride reveals a variation of yields from 20 to 90 percent under apparently similar conditions. At times, the reaction requires a lengthy induction period and then reaches an uncontrolable velocity. The main reason for this irregular behavior may be the presence of humidity in the ether, which causes the formation of a film of oxides on LiH particles. So, the purity requirements for LiH and ether ought to be strict. A complete analysis of the products from several experiments revealed other factors which influence the yield if diborane. Research showed that the reaction of LiH with the etherate of boron trifluoride cannot be presented in the form of one equation, but represents a series of simultaneous reactions with consecutive stages.

Besides reactions (1) and (2), not counting intermediate stages, the following reactions are possible:

$$4\ LiH + BF_3 \cdot (C_2H_5)_2O \longrightarrow LiBH_4 + 3\ LiF \qquad (3)$$

$$BF_3 + LiF = LiBF_4 \qquad (4)$$

$$BF_3 + 3\ LiBH_4 = B_2H_6 + 3\ LiF. \qquad (5)$$

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Preparation of diborane with varying $BF_3 \cdot (C_2H_5)_2$ / LiH ratios [3].

Table 19

Experiment	Used, g		BF_3 / LiH	Yield of B_2H_6		Yield of $LiBH_4$	Yield of $LiBF_4$
	LiH	BF_3		in % from BF_3	in % from LiH	in % from BF_3	in % from BF_3
1	4.2	21.8	1:3.5	49	43.5	not determ.	not determ.
2	4.55	12.7	1:6.3	53	40	30.7	"
3	2.4	14.0	1:3	19.7	23.79	0	"
4	5.1	28.36	1:3.2	25	22.6	3.83	"
5	2.7	11.22	1:4.2	43.4	30.5	0	"
6	3.2	18.7	1:3	28.9	27.7	0	"
7	7.5	42.6	1:3.1	39.1	33	0	"
8	22	118	1:3.3	46.5	42.2	0	"
9	13	71	1:3.2	44.4	41.1	0	40
10	12	71	1:3	42.9	42.9	0	44.6
11	10	42.6	1:4.1	58.72	42.30	not determ.	not determ.
12	7.5	42.6	1:3	47.53	47.53	"	"
13	2.7	28.24	1:1.7	22.46	30.5	0	61.24
14	1.2	28.24	4:3	23.02	62.1	0	46.13
15	5.0	14.12	1:6	not determined		15.2	not determ.
16	6.7	28.4	1:4.1	63	45.0	22.7	traces

Order of reaction.

1	Etherate strongly diluted in ether. Extensive induction period. Hydride is added to BF_3 etherate.
2	Etherate is diluted in 25 ml of ether. Entire hydride added.
3	Hydride added to undiluted BF_3 etherate.
4	ditto
5	Gradual addition of hydride to etherate. Mixture stands 24 hours; 20 ml of ether added during the reaction.
6	ditto
7	Hydride gradually added to etherate; mixture periodically heated.
8	Etherate added in two stages; hydride gradually added.
9	ditto
10	Gradual alternative addition of ether and hydride.
11	ditto (drops)
12	Etherate gradually added to suspension of LiH in 30 ml ether
13	ditto
14	ditto
15	Reaction conducted at 0°; etherate gradually added to suspension of hydride in 10 ml ether.
16	Hydride suspension in 60 ml ether at 15° gradually added to BF_3 etherate.

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The conversion of boron trifluoride proceeds in three directions: formation of diborane, lithium borohydride, and lithium borofluoride. Taking into consideration solubility in ether of the obtained products:

B_2H_6 .... 1.1g/100g

$LiBF_4$ 1.9g/100g

$LiBH_4$ 3.0g/100g

LiF 0.05g/100g

also data from the above quoted experiments, which confirm the fact that the gaseous phase contains diborane only, it can be assumed that the solid phase, after the elimination of ether, can contain along with an excess of unreacted LiH, lithium fluoride, and boron containing compounds: lithium borofluoride, and lithium borohydride.

The reaction can be directed towards a greater or smaller relative yield of diborane, depending on the temperature, dilution in ether, and the ratio and order of the addition of initial substances.

When the reaction takes place at room temperature, and with a relatively excessive amount of LiH, the mixture heats to 25 — 35° and leads principally to the formation of diborane. Lithium borohydride did not accumulate in the ether solution. Still, a considerable amount of boron remains in the solid sediment in the form $LiBF_4$ and the lithium hydride is not fully used up.

A considerable excess of boron trifluoride not only lowers the yield in relation to boron, but it also lowers the yield in relation to the consumption of lithium hydride. It has been found that far better results were obtained for conditions used in the second series of experiments (table 20) with a ratio of BF_3 : LiH higher than that

indicated by the stoichiometry of the equation (1), and with a gradual addition of the etherate of boron trifluoride to the entire portion of lithium hydride, accompanied by vigorous stirring. Here, lithium borohydride does not form, and the yield of diborane increases both in respect to the amount of boron consumed, and to the amount of lithium hydride.

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Reaction in presence of excess of etherate of boron trifluoride [3]. Table 20.

Experiment	used, in g		$\frac{BF_3}{LiH}$	yield of diborane		yield	
	$BF_3(C_2H_5)_2O$	LiH		in % to B	in % to LiH	$LiBH_4$ in % to B	$LiBF_4$ in % to B
1	46.15(0.325)	6.4(0.8)	1:2.45	53.1	65.3	0	18.0
2	49.7(0.35)	5.4(0.675)	1:2	60.82	96.34	0	37.5
3	60.3(0.425)	6.4(0.8)	1:2	57.0	88.1	0	37.5
4	42.3(0.30)	6.4(0.8)	1:2.7	83.45	94.6	0	11.1

Equations of the reaction:
for experiments nr. 1 .... $6\ LiH\ 2.44\ BF_3(C_2H_5)_2O \rightarrow B_2H_6\ \ 0.44\ LiBF_4 + 5.56 LiF + 2.44 (C_2H_5)_2O$

nr. 2 ... $6\ LiH + 3.2\ BF_3(C_2H_5)_2O \rightarrow B_2H_6 + 4.8\ LiF + 1.2\ LiBF_4 + 3.2\ (C_2H_5)_2O$

nr. 3 ... ditto

nr. 4 ... $6\ LiH + 2.25\ BF_3(C_2H_5)_2O \rightarrow B_2H_6 + 5.75\ LiF + 0.25\ LiBF_4 + 2.25\ (C_2H_5)_2O$

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In this case the reaction does not follow equation (1) nor (2), but the equation in which the number of moles of the etherate of boron fluoride varies in the range of 2.25 — 2.8.

Time curves for the evolution of diborane have clearly marked inflection points A (fig. 1) [3]. This indicates that the reaction takes place in two stages during the gradual addition of the etherate; during the first stage, characterized by a great excess of LiH, diborane evolves fairly slow, due to an accumulation of active intermediate products, probably also lithium borohydride, without detectable formation of lithium borofluoride. The second stage includes the interaction of new portions of the etherate with the remaining lithium hydride, and with the active intermediate products of the reaction, among others, with lithium borohydride. This stage of the reaction shows the major increase in diborane, what is evident from the sharp rise of the curve (fig. 1).

In both stages, the reaction probably has a step-wise mechanism with the formation of intermediate products, $LiHBF_3$, $LiBH_2F_2$, and $LiBH_3F$.

The last two compounds can form diborane, since their molecules contain a quasi ready borine group BH_3:

$$2\ LiBH_3F \longrightarrow B_2H_6 + 2\ LiF$$

$$2\ LiBH_3F + 2BF_3\cdot(C_2H_5)_2O \longrightarrow B_2H_6 + 2\ LiBF_4,$$

$$3\ LiBH_4 + BF_3\cdot(C_2H_5)_2O \longrightarrow 2\ B_2H_6 + 3\ LiF.$$

A parallel reaction takes place, especially in the first stage, of diborane with excess LiH:

$$2\ LiH + B_2H_6 \longrightarrow 2\ LiBH_4$$

and at the same time, in case of excess boron fluoride, reaction (4). Further, in the initial stage of the reaction, when temperature of the mixture reaches 40°, disproportionation of intermediate products is possible:

$$2\ LiHBF_3 \longrightarrow LiBH_2F_2 + LiBF;$$

$$3\ LiBH_2F_2 \longrightarrow B_2H_6 + LiBF_4 + 2\ LiF\ ;$$

$$4\ LiBHF_3 \longrightarrow LiBH_4 + 3\ LiBF_4\ etc.$$

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These reactions to a certain degree show the complexity of the studied reaction. A conclusion can be drawn, that in order to achieve the maximum yield of diborane, the reaction should run with an excess of LiH in the initial stage, and at the same time, a larger amount of the etherate of boron trifluoride should be used than indicated by the stoichiometry of equation (1). This is achieved by conditions given for experiment nr.4 in table 20.

Experiment nr. 4 (table 20) is carried out as follows: 21.3 g etherate of boron trifluoride are rapidly added to a suspension of 6.4 g (0.8 mole) of LiH in 15 ml of absolute ether. The mixture is stirred at the same time by means of an electromagnetic agitator. The remaining amount of the etherate is gradually added so, that an even evolution of diborane continues. The total amount of the etherate added was 42.3 g (0.30 mole). Continued addition of etherate did not give any diborane. Ether is added to the reacting mixture when needed (15 ml, three times). The obtained diborane is captured by dry pyridine. The pyridine traps were periodically exchanged, in order to study the amount of diborane generated in reference to time (fig. 1) The yield of diborane related to the etherate of boron trifluoride, according to equation (1) equals 83.4 percent, and to LiH, it is 94.6 percent.

This procedure can serve as a scheme for the preparation of pure diborane, with a high and even yield in relation to lithium hydride and etherate of boron trifluoride which were used in the reaction.

The best results are obtained from the hydrogenation of boron halides [12] [8]. Therefore, it would be best to use hydrogen directly in the preparation of large quantities of diborane.

For this purpose, boron chloride and bromide were hydrogenated in a strong electrical discharge. Hydrogen flows through liquid $B\,Cl_3$ at -40° forming a gaseous mixture $BCl_3 + H_2$, which at a lower pressure (10 mm) passes through the electrical-discharge zone (12 — 15 kv). The mixture obtained consists of H_2, HCl, BCl_3, B_2H_5Cl, and boranes. It is condensed for the separation of hydrogen, and distilled at 2 atm.

During distillation, diborane chloride B_2H_5Cl decomposes into diborane and boron chloride. Fractions richer in boranes are distilled again.

Use of boron bromide instead of chloride gives good results. The yield of diborane in relation to reacted BCl_3 can reach 60 - 75 percent and, for BBr_3 up to 80 percent.

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Various quantities of other boranes are formed depending on the reagent ratios and on how long the mixture is kept in the discharge zone.

At the present time a simpler method is being used. It is the direct hydrogenation of boron chloride and bromide in the presence of granulated aluminum, or other metals which bind bromine and chlorine:

$$2\ BCl_3 + 3\ H_2 + 2\ Al \longrightarrow B_2H_6 + 2\ AlCl_3.$$

The best conversion of boron chloride into diborane is obtained at 450° for the molar ratio $BCl_3 : H_2 = 1 : 6$.

Other boranes are prepared by the thermal decomposition of diborane [12]. Under various conditions of pyrolysis, diborane can produce stable, or unstable pentaborane, solid boranes, and also tetraborane.

Pyrolysis is conducted at 175 - 200°, duration of contact of diborane with heated reactor 2.7 - 3.3 sec, and pressure 102 - 106 mm. The first run did not show appreciable conversion. The unreacted diborane was recirculated, and the entire process lasted up to 16 - 20 hours.

In some instances diborane was diluted with hydrogen, or nitrogen, as shown in table 21.

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Effect of hydrogen and nitrogen on diborane conversion during pyrolysis [12].

Table 21.

Ratios		Temp. °C	Conversion of B_2H_6, %	Reaction products, mol.%			
$H_3 : B_2H_6$	$N_2 : B_2H_6$			B_4H_{10}	B_5H_9	B_5H_{11}	Solids
0	0	174	70.9	4	3	85	8
0	0	200	92.4	4	43	39	14
0	0	225	95.6	3	63	3	31
1.0	0	200	88.6	3	40	50	7
1.0	0	225	93.0	0	81	0	19
5.0	0	175	23.3	4	0	88	8
5.0	0	200	57.3	5	28	62	5
5.0	0	225	79.0	1	78	10	11
5.0	0	225	83.3	4	82	0	17
4.9	0	225	82.1	0	86	0	14
4.9	0	225	98.7	0	37	0	63
0	5.0	185	52.9	12	0	77	0
0	5.0	211-216	88.3	3	33	47	17
0	5.0	225-227	94	5	58	7	30

The best yield of stable pentaborane was obtained (to 80 percent) at the temperature of 225°, at which a high conversion of diborane was observed. Unstable pentaborane is formed at lower temperatures (e.g., at 175°). The use of hydrogen in the pyrolysis increases the yield of B_5H_9 and decreases the formation of solid boranes. Dilution with nitrogen does not give good results. Increasing the temperature of the reaction to 250° increases the yield of solid boranes to 30 - 50 percent.

The effect of the time of contact of diborane with the heated reactor upon the conversion and on the yield of reaction products is shown in table 22.

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Effect of the time of contact on the conversion and on the yield of boranes in the pyrolysis of diborane [12].

Table 22.

Ratio $H_2 : B_2H_6$	Temp. °C	Time of contact, sec	Number of runs	Conversion, %	Reaction products, mol% B_4H_{10}	B_5H_9	B_5H_{11}	Solids
0	175	3.3	150	70.9	4	3	85	8
0	175	20.8	24.1	66.6	4	18	67	11
5.0	200	3.2	15	57.3	5	28	62	5
4.9	200	6.8	105	70.7	6	56	33	5
4.9	225	3.0	169	82.1	0	86	0	14
4.9	225	13.0	36.4	87.4	0	78	0	22
1.0	228	3.0	9.4	72.1	2	55	32	11
1.0	222	6.7	4.1	69.5	2	62	17	19

The conversion of diborane depends only on the total time of contact with the reactor, provided other conditions are maintained equal, for the number of runs performed. The increase of the total contact time causes an increase in the yield of stable pentaborane B_5H_9 and of solid boranes. Additions of hydrogen bromide and chloride, and of boron halides, do not reveal any real effect.

The pyrolysis of diborane is an exothermic reaction, since the temperature can rise spontaneously even when electric heating is discontinued.

Along with the development of methods for the preparation of boranes from the pyrolysis of diborane, the kinetics of the mechanism were also studied. The following scheme was proposed for the conversion of diborane into pentaborane:

$$2\ B_2H_6 \rightleftharpoons 2\ BH_3$$

$$B_2H_6 + BH_3 \longrightarrow B_3H_7 + H_2$$

$$B_3H_7 + B_2H_6 \longrightarrow B_5H_{11} + H_2$$

$$B_5H_{11} \nearrow B_5H_9 + H_2$$

$$B_5H_{11} \searrow B_2H_6 + \text{higher boranes.}$$

In the first phase of the reaction diborane dissociates to unstable borine, which in the second phase, reacts with diborane to give the hypothetical triborane, and the latter with diborane forms unstable pentaborane, from which evolve stable pentaborane and decomposition products.

The kinetics of diborane pyrolysis was studied at a temperature from 85 — 163° and pressure 25 — 200 mm. The rate of diborane decomposition during pyrolysis in relation to concentration and temperature is shown in table 23. Besides total pressure, the partial pressure of hydrogen was measured. For this purpose, other products of the reaction were eliminated by freezing.

Rate of diborane pyrolysis in a closed vessel;
vol. 211.8 ml. [12]

Table 23.

Temp. °C	Concentration of B_2H_6 (mole/l).10^{-2}	Rate of pressure increase (mole/l hour)·10^4
89.6	2.718	3.8
"	2.092	2.7
"	1.536	1.6
100.0	2.153	7.4
100.0	2.188	8.0
99.9	2.097	7.3
99.9	1.310	3.7
99.9	1.281	3.5
100.0	0.437	0.73
110.1	2.036	19.3
"	1.275	9.3
"	0.4334	1.9
120.1	0.6332	7.1
"	0.4191	3.1
"	0.2165	1.1
130.1	0.4008	9.5
"	0.2119	2.9

The rate of pressure increase w_p in the pyrolysis of B_2H_6 is determined from the equation:

$$w_p = KC_o^n$$

where C_o = initial concentration of B_2H_6

n = order of reaction equal 1.49 at 89.6 — 110°

K = reaction-rate constant varying in the given temperature range from 0.085 to 0.66.

The order of the reaction increases with the increase of temperature, and reaches 1.89 at 130.1°. Activation energy of the B_2H_6 pyrolysis obtained from the variations of the reaction-rate constant with increased temperature from 120.1 to 130.1° equals 27.4 ± 0.7 kcal/mole.

Tetraborane B_4H_{10} can be produced by heating a mixture of hydrogen and unstable pentaborane [12] preserving the ratio of 10 : 1, at 100° for 10 minutes:

$$2\,B_5H_{11} + H_2 \longrightarrow 2\,B_4H_{10} + B_2H_6.$$

The yield is ca 85 percent.

Tetraborane B_4H_{10} can also be prepared [12] by passing diborane through a heated furnace at 180°, and then through a cooling trap (-115°) to condense reaction products and unreacted diborane. Diborane is separated by low temperature distillation.

Several methods for the preparation of tetraborane proved to be low in yield, and requiring complicated apparatus. The method of obtaining tetraborane from metal borides appears to be much simpler, and yielding primarily the desired borane.

Mikheeva and Markina [6] studied the sintering of magnesium with boric anhydride in order to establish the quantitative relations of components in the sintered mixture assuring the maximum yield of tetraborane ensuing from acid decomposition.

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Data from the systematic study of this reaction are still unpublished, although the method is often applied. The optimum ratios for magnesium and boric anhydride are widely divergent. In order to determine this ratio, the reaction was studied in a wide range of varying content of both reagents. The composition of the mixtures varied in an interval from 0 — 100 percent of each component. Results are shown in the following table.

Yield of boranes from the products of the interaction of boric anhydrides with magnesium [6].

Table 24.

Nr.	Composition in at. %		Composition in wt. %		Yield of boranes in % of B
	B_2O_3	Mg	B_2O_3	Mg	
1	100	0.	100	0	0
2	95	5	98.17	1.83	0.020
3	90	10	96.27	3.73	0.025
4	85	15	94.17	5.83	0.030
5	80	20	91.96	8.04	0.066
6	75	[illegible]	89.56	10.44	0.068
7	70	30	86.98	13.02	0.050
8	65	35	84.16	15.84	0.113
9	60	40	81.12	18.88	0.166
10	57.2	42.8	79.29	20.71	0.209
11	54	46	77.07	22.93	0.248
12	51.2	48.8	75	25	0.104
13	45	55	70.03	29.92	0.012
14	40	60	65.60	34.40	0.
15	35	65	60.64	39.36	0
16	30	70	55.10	44.90	0
17	25	75	48.82	51.18	0.115
18	20	80	41.71	58.29	0.333
19	14.3	85.7	32.32	67.68	1.312
20	10	90	24.13	75.87	0.901
21	5	95	13.09	86.91	0.456
22	0	100	0	100	0

The yield of boron in the form of tetraborane as a function of the B_2O_3: Mg ratio in the sinter is shown in the figure 2. It is evident that the quantity appears to be in maximum for the composition: 67.68 at. percent of Mg and 32.32 at. percent of B_2O_3, or 85.7 at. percent Mg and 14.3. percent of B_2O_3, that is for the weight ratio Mg : B_2O_3 = 2 : 1, or the atomic ratio Mg : B_2O_3 = 6 : 1, which is in full agreement with the equation: $B_2O_3 + 6\ Mg = B_2Mg_3 + 3\ MgO$.

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A small relative maximum of the yield of boranes is noted for the content: 46 at. percent Mg and 54 at. percent B_2O_3.

A parallel set of experiments for the decomposition of magnesium boride with different acids revealed the preference for phosphoric acid over sulfuric and hydrochloric acids. Table 25 gives results for the determination of the yield of tetraborane from identical samples of magnesium boride treated with 8 N hydrochloric, sulfuric, and phosphoric acids, at 50°.

Yield of tetraborane from treatment with various acids [6]

Table 25.

8 N acid	Yield of boranes per B in %
hydrochloric	2.40 -- 4
sulfuric	1.16 -- 1.5
phosphoric	14.2 -- 16.1

Decomposition of magnesium boride obtained from a sinter in the form of B_2Mg_3, and treated with phosphoric acid, shows a yield of tetraborane from 90 — 95 percent of total boron from the condensation of volatile boranes, that is 12 — 14 percent of the total boron used in the preparation of magnesium boride.

The multiple confirmation of the maximum yield of tetraborane from the boron-magnesium sinter with B : Mg $\approx$ 2 : 3 indicates the existence of the simplest form of magnesium boride, the B_2Mg_3.

Pentaborane [12] is obtained by passing diborane through a tube at 250°, under pressure of 120 mm, and velocity of 50 ml/min. Then B_5H_9 shows a yield of 56 percent, and B_5H_{11} a yield of 26 percent.

Unstable pentaborane shows a better yield when diborane is passed through a tube heated to 115° with such a velocity as to reach a 2 min time of contact. Unreacted diborane is separated and recirculated. The conversion of diborane after several recirculations reaches 90 percent.

Decaborane [12] $B_{10}H_{14}$ is prepared by heating diborane at 250°.

Diborane heated to 160° in a closed vessel, under pressure slightly higher than normal, shows a yield of ca 30 percent of $B_{10}H_{14}$.

Borane derivatives.

The chemistry of boranes [12] appears to be a new, and interesting field of inorganic chemistry, both from the theoretical and applied aspects. Boranes are of great interest in organic chemistry, since they readily form various boron organic compounds.

At the same time, more scientists are attracted to the study of boranes as an interesting field in the general chemistry of boron.

Boranes [8], like silanes and hydrocarbons, do not add free Cl and Br, but both halides substitute the H atoms.

In presence of 1) an excess of borane:

$$B_2H_6 + Hal_2 = B_2H_5Hal + HHal,$$

various derivatives are formed with one or more hydrogen atoms being substituted;

2) an excess of halide:

$$B_2H_6 + 6\ Hal_2 = 2\ BHal_3 + 6\ HHal.$$

In presence of aluminum halides, boranes, like silanes, exchange hydrogen for a halide. The same takes place in their interaction with free hydrogen halides:

$$B_2H_6 + HI = B_2H_5I + H_2.$$

The product of this reaction is a colorless fluid, solidifying at -110°. Sodium amalgam separates iodine, and leads to the formation of B_4H_{10}:

$$2\ B_2H_5I + 2\ Na = B_4H_{10} + 2\ NaI.$$

This is an analog of the reaction of hydrocarbon halo derivatives with metallic Na.

Diborane monobromide B_2H_5Br is the best known halo derivative. It is a colorless gas with m.p. -104°

b.p. $+10^\circ$

shows a tendency to spontaneous decomposition into B_2H_6 and BBr_3 :

$$6\ B_2H_5Br = 2\ BBr_3 + 5\ B_2H_6.$$

Even a more rapid decomposition is shown by the corresponding chlorides, and products containing more than one halide atom in the molecule.

Diborane B_2H_6 agitated with K, or Na, amalgam, forms a white crystalline addition product $K_2B_2H_6$ which is stable in dry air, sublimates at 400°, with partial decomposition, hydrolyzes slowly in water:

$$K_2B_2H_6 + H_2O = 2\ KBO_2 + 7\ H_2.$$

Analogous compounds of other boranes were also prepared: $K_2B_4H_{10}$, and $K_2B_5H_9$. Note that boranes in contact with free alkali metals do not form such addition products. Diborane also does not react with KH.

These salts of boranes appear to be stable compounds: $Na_2B_2H_6$, $K_2B_2H_6$. CaB_2H_6 [12]. The first two sublimate in vacuum without complete decomposition. They are stable in dry air, but hydrolyze easily in water. Tetraborane and pentaborane give salts of alkali metals of the type: $Me_2B_4H_{10}$, and $Me_2B_5H_9$, as mentioned before.

Metal borohydrides [8] [12].

The discovery of metal borohydrides of the type $Me^{I}BH_4$, $Me^{II}(BH_4)_2$, etc., proved to be extremely interesting. Many metal borohydrides distill without decomposition, or easily sublimate, so that they can be obtained in a state of high purity. They are used as reducing agents, and as source of hydrogen.

Certain borohydrides are well known, e.g., lithium, beryllium, and aluminum borohydrides. Recently, properties of many other borohydrides were also described.

The double hydrides $LiBH_4$, $NaBH_4$ and $LiAlH_4$, are recognized as good selective reducing agents. [15] Ordinarily, they do not hydrogenate the carbon - carbon double bond, what permits the preparation of unsaturated alcohols, amines, and hydrocarbons, from the corresponding ketones, aldehydes, acid derivatives, nitro compounds, and halo derivatives of unsaturated hydrocarbons.

Most of these reactions occur at room temperature, and normal pressure, giving good yields and do not result in by-products.

Interaction of diborane B_2H_6 with Al, Be, and Li alkyl derivatives gives the following compounds: $Al(BH_4)_3$, $Be(BH_4)_2$, and $LiBH_4$.

Aluminum borohydride $Al(BH_4)_3$ is a fluid with a m.p. -65° and b.p. $+45^\circ$. Its density, surface tension, and viscosity, can be computed from the following equations:

$$d = 0.7866 - 0.000793\ T$$

$$\gamma = (61.0 - 0.130\ T)\ d^{2/3}$$

$$\eta = 23 \cdot 10^{-3}\ d^{1/3}\ e^{1291d/T}.$$

Physical properties of aluminum borohydride $Al(BH_4)_3$ [12].

Table 26

Temp. °K	Density g/cm³	Viscosity in millipoise	Temp. °K	Surface tension dyne/cm
209.3	0.6203	9.28	209.6	24.6
217.3	0.6141	7.58	216.2	23.8
228.9	0.6047	5.91	227.4	22.6
239.6	0.5966	4.69	238.3	21.3
261.7	0.5881	3.39	248.9	20.0
265.0	0.5805	3.12	258.7	19.0
274.1	0.5690	-	260.3	18.8
287.4	0.5588	2.34	263.7	18.6
306.6	0.5445	1.93	286.8	16.0
-	-	-	305.1	14.3

Beryllium borohydride $Be(BH_4)_2$ is a solid which sublimates at 91°.

Aluminum and beryllium borohydrides have a weak ionic character and vigorously ignite when exposed to air. As all other borohydrides, they hydrolyze easily in water generating hydrogen, and add one molecule of trimethylamine.

Lithium borohydride $LiBH_4$ has a strong saltlike ionic character, with Li^+ cation and $[BH_4]^-$ anion. It is stable in dry air in contrast to other borohydrides. When heated to ca 275° $LiBH_4$ melts, and decomposes. Treated with HCl it gives LiCl, H_2, and B_2H_6.

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Lithium borohydride sometimes shows loss of activity due to partial hydrolysis [2]. In order to determine the effect of hydrolysis on the activity of $LiBH_4$, several samples of the borohydride were used. It was detected, that the degree of hydrolysis varies with changing conditions in the medium. Experimental data show that so-called hypoborates, products of the interaction of diborane and tetraborane with KOH, can be regarded as separate phases of the hydrolysis of potassium borohydride. The complete hydrolysis of alkaline borohydrides requires an acidic medium, and special catalysts. It would be very interesting to be able to prove the stepwise character of the hydrolysis of lithium borohydride, a compound, which is less polar than borohydrides of alkali metals.

Effect of temperature and catalyst on the hydrolysis of $LiBH_4$ [2].

Table 27

Sample of hydride, g	% of H generated by addition of H_2O		H generated by add. of acidified $NiCl_2$ solution	Ratio $H_I : H_{II} : H_{III}$
	20° H_I	100° H_{II}	H_{III}	
0.0196	4.14	-	18.03	$H_I : H_{III} = 1 : 4.45$
0.0180	4.63	-	17.78	$H_I : H_{III} = 1 : 3.8$
0.0220	4.50	(6.4 at 60 - 80°)	17.05	$H_I : H_{III} = 1 : 3.8$
0.0230	4.60	10.56	17.92	$H_I : H_{II} : H_{III} = 1 : 2.3 : 3.9$
0.0366	3.381	7.78	18.1	$H_I : H_{II} : H_{III} = 1 : 2 : 4.5$

The ratio of quantities of hydrogen generated at 20°, 100°, and the total possible H from the hydrolysis, is 1 : 2 : 4. Slightly acidified and highly diluted solution of $NiCl_2$ or $Ni(NO_3)_2$, causes immediate generation of hydrogen and the formation of a black precipitate of nickel boride. All of the active hydrogen from lithium borohydride is generated (18.49 percent). The same is observed in the presence of cobalt salts ($CoCl_2$). Copper salts ($CuSO_4$), and silver salts ($AgNO_3$) are less active.

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The hydrolysis proceeds less rapidly in an alkaline medium. A concentrated solution of ammonia, 0.1 and 4 N solutions of sodium hydroxide cause partial generation of hydrogen (see table 28)

Hydrolysis of $LiBH_4$ in an alkaline medium [2].

Table 28

Medium	Active hydrogen, %	H_2 generated when $NiCl_2$ added, %
Conc NH_4OH	0.71	16
0.1N NaOH	2.1	9.8
4 N NaOH	0.65	6.34

A subsequent addition of nickel salt solutions ($NiCl_2$) to alkaline solutions, causes a supplementary generation of hydrogen, but does not result in its complete generation. The ammoniacal solution of lithium borohydride, when heated with a nickel salt solution, gives a perfect metallic mirror on the walls of the test tube.

Hydrogen and boron contents in products of $LiBH_4$ hydrolysis [2].

Table 29

	$LiBH_4$	$LiBH_3OH$	$LiBH_2(OH)_2$	$LiBH(OH)_3$
H, %	18.49	8.00	3.75	1.44
B, %	49.65	28.64	20.11	15.50

The stepwise character of the hydrolysis can be seen if we compare experimental data obtained from the decomposition of lithium borohydride under various conditions (tables 27 and 28) with the composition of compounds which appear to form the intermediate stages of hydrolysis (table 29).

One of the four hydrogens of lithium borohydride separates at 20° and $LiBH_3OH$ is formed, which is stable for these conditions. Further heating to 100° brings substitution of the second hydrogen atom by a hydroxyl group, with the formation of the next stage of hydrolysis, $LiBH_2(OH)_2$. An acidified solution of $NiCl_2$ completes the hydrolysis with the formation of $LiB(OH)_4$ or $LiBO_2$ $2H_2O$, where all four hydrogen atoms are replaced by hydroxyl groups.

The white precipitate which forms after the solution of $LiBH_4$ in ether has a composition (2.60 — 2.70 percent of active H, and 18.0 — 22.9 percent of B) which corresponds to the composition of the equivalent mixture of $LiBH_2(OH)_2$ and $LiBH(OH)_3$. It liberates hydrogen only in water heated to 100° or after addition of an acidified solution of $NiCl_2$.

Sodium borohydride $NaBH_4$ [15] attracts attention as a reducing agent, since it alone of all the hydride, forms aqueous solutions which are relatively stable at room temperature. It liberates free metals or their borides from solutions of a series of salts.

Sodium borohydride does not reduce acids, esters, anhydrides, mitriles, and nitro compounds, but reduces aldehydes, ketones, and acid chlorides to alcohols.

$NaBH_4$ [8] is stable up to 400°, well soluble in cold water, and contrary to $LiBH_4$, it reacts with H_2O very slowly. It reacts rapidly, when heated, or in presence of acids.

The BH_4^- ion contained in the saltlike borohydrides has the structure of a regular tetrahedron with a B atom in the center. Other compounds of this type have apparently structures based on H bonds between BH_3 molecules and hydrides of corresponding elements.

Other borohydrides, with properties similar to those of $Al(BH_4)_3$, were also prepared. Their general formula is:

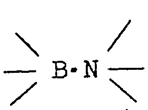
$$E(BH_4)_4$$

e.g.: $Th(BH_4)_4$, $Hf(BH_4)_4$, $Zr(BH_4)_4$, $Ti(BH_4)_4$.

Diborane derivatives containing nitrogen [19].

Diborane forms nitrogen containing derivatives from the interaction of compounds with trivalent nitrogen and diborane, or its organic substituted derivatives. Diborane behaves as a combination of two BH_3 groups which, at low temperatures, form products of borine addition to a nitrogen atom. This is also true for diborane organic substituted derivatives: monoethyl- , trimethyl- , and tetramethylborine which form products of addition of mono- and dimethylborine to compounds of the type:

$$CH_3H_2BNR_3 \qquad (CH_3)_2HBNR_3$$



Products result from the formation of the coordination linkage with the completion of the electron shell of the B atom at the expense of the unseparated pair of valence of the N atom.

Diborane and its methyl derivatives enter more complex reactions with amines and ammonia, forming a series of N-containing diborane derivatives in which there is a covalent B — N bond, and the complexing tendency of the B atom is evident in its capacity for **copolymerization** and addition.

Three main groups of compounds formed by the interaction of diborane and of its methyl derivatives with N-containing bases, can be classified as follows:

1) Borazanes - diborane derivatives from the addition of borine and of its methyl derivatives to N-containing bases.

2) Borazenes - from the thermal conversion of addition products at moderate temperatures ($H\uparrow$ or $CH_4\uparrow$)

3) Borazines - from the thermal conversion of addition products at higher temperatures; mostly in the form of trimers of borazole and of its derivatives.

Diborane nitrogen compounds are not well known and their terminology is not yet established.

Borazanes.

Diborane and its methyl derivatives give the following borazanes from their reaction with (bases + N):

BH_3NR_3	BH_3NHR_2
$BH_2CH_3NR_3$	$(BH_2CH_3NHR_2)$
$BH(CH_3)_2NR_3$	$(BH(CH_3)_2NHR_2)$
BH_3NH_2R	BH_3NH_3
$(BH_2CH_3NH_2R)$	$BH_2CH_3NH_3$
$BH(CH_3)_2NH_2R$	$BH(CH_3)_2NH_3$

R = hydrocarbon radical.

Their formation occurs according to the equations:

a) $B_2H_6 \longrightarrow 2\ BH_3$

$(H_3C)_2B_2H_4 \longrightarrow 2\ CH_3BH_2$ etc.

b) $BH_3 + NR_3 \longrightarrow BH_3NR_3$

$BH_3 + NHR_2 \longrightarrow BH_3NHR_2$

$CH_3BH_2 + NR_3 \longrightarrow CH_3BH_2NR_3$

$CH_3BH_2 + NHR_2 \longrightarrow CH_3BH_2NHR_2$ etc.

Known borazanes and their properties [19].

Table 30

Compound	m.p. °C	b.p. °C	decomposition temperature °C
$(BH_3NH_3)_2$	90	nonvolat.	above 90
$BH_3NH_2CH_3$	5 - 10	nonvolat.	room temperature
$BH_3NH(CH_3)_2$	10 - 12	nonvolat.	room temperature
$BH_3N(CH_3)_3$	94	170	above 125
$CH_3BH_2NH_3$	-	-	50
$(CH_3)_2BHNH_3$	-	-	above 35
$CH_3BH_2N(CH_3)_3$	0.8	177	200
$(CH_3)_2BHN(CH_3)_3$	-16	172	70
$C_6H_5NBH_3$	10 - 12	-	155 - 160
C[illegible]H_7NBH_3	95 - 96	-	118

Borazenes.

All theoretically possible borazenes can be represented by the general formulas:

H_2BNR_2	H_2BNHR
(CH_3HBNR_2)	(CH_3HBNHR)
$(CH_3)_2BNR_2$	$(CH_3)_2BNHR$

$$H_2BNH_2$$
$$CH_3HBNH_2$$
$$(CH_3)_2BNH_2$$

R = hydrocarbon radical.

Borazenes are formed from borazanes according to the following equations:

$$H_3BNHR_2 = H_2 + H_2BNR_2$$

$$CH_3H_2BNHR_2 = H_2 + CH_3HBNHR_2$$

$$H_3BNH_2R = H_2 + H_2BNHR$$

$$(CH_3)_2HBNH_3 = H_2 + (CH_3)_2BNH_2 \quad \text{etc.}$$

Properties of the known borazenes are shown in table 31.

Known borazenes and their properties [19].

Table 31

	molecular form at room temp.	m.p. °C	b.p. °C
$H_2BN(CH_3)_2$	dimer	73.5	-
H_2BNH_2	polymer	-	-
$(CH_3)_2BN(CH_3)_2$	monomer	92.2	65
$(CH_3)_2BNHCH_3$	monomer	-	38.3
$(CH_3)_2BNH_2$	monomer		4 (monom. liquid)
	dimer 9		
$H_2BN(C_2H_5)_2$	dimer	white crystalline substance	
$H_2BN(iso\text{-}C_3H_8)_2$	properties not yet determined		
$(CH_3)_2BNHC_6H_5$	transparent colorless liquid		
$H_2BN(SiH_3)_2$	monomer	-	-
	dimer		
$H_2BNCH_3NCH_3B_2H_2$	monomer	0.4	-
H_2BNHCH_3	trimer	properties are not known	

The chemical activity of borazenes is governed by the form of molecules. The dimeric molecule is inert towards water, hydrogen halides, diborane, etc., while the monomeric molecule appears to be unsaturated, and readily entering addition reactions. Therefore, monomeric borazenes react already at room temperature, and dimers only at higher temperatures, when evidently occurs depolymerization of molecules.

The reaction of borine addition to monomeric borazene H_2BNH_2 is of special interest. It results in $B_2H_5NH_2$ ordinarily called aminodiborane. N-substitution derivatives of borazene H_2BNH_2 give N-substitution derivatives of aminodiborane. This is observed when borazane comes into contact with diborane at a corresponding temperature.

For instance, the reaction with dimethylaminoborine at 135° gives simethylaminodiborane:

$$2\ H_2BN(CH_3)_2 + B_2H_6 = 2\ B_2H_5N\cdot(CH_3)_2\ .$$

Physicochemical properties of aminodiborane and of its N derivatives. [19].

Table 32

Compound	m.p. °C	b.p. °C	density at 0°C
$B_2H_5NH_2$	-66.5	76.2	0.6486
$B_2H_5NHCH_3$	-	66.8	-
$B_2H_5N(CH_3)_2$	-54.6	50.3	0.6456
$B_2H_5N(SiH_4)_2$	-68.8 — 69.4	54	-
$B_2H_5NSiHCH_3$	-39	51	-

Aminodiborane and all its known derivatives show thermal instability, except dimethylaminodiborane. It is a mobile liquid which decomposes slowly during storage [12]. It is obtained by passing diborane over diborane diammoniate at 88°:

$$B_2H_6\cdot 2NH_3 + B_2H_6 \longrightarrow 2\ B_2H_5NH_2 + 2\ H_2\ .$$

It is also found as a by-product in the synthesis of borazole.

Electron diffraction studies show that its crystal structure resembles dimethylamine. Chemically, it behaves like an amide in which two acidic borine groups BH_3 are linked with an $>$NH group. Diborine amine can add one ammonia molecule to form an ammoniate:

$$B_2H_5NH_2 + NH_3 \longrightarrow NH_3\cdot B_2H_5NH_2\ .$$

This substance differs from diborane diammoniate $B_2H_6\cdot 2NH_3$ in its hydrogen content, and obviously in structure. Nevertheless, when rapidly heated to 200°, aminodiborane ammoniate, as well as $B_2H_6\cdot 2NH_3$, give borazole with a 45 percent yield.

Borazines

Borazenes, with hydrogen atoms at N, lose H or CH_4 molecules during heating: at 180 — 200° for H

300 — 450° for CH_4 .

These reactions result in the formation of borazines:

$$H_2BNHR = H_2 + BHNR$$

$$CH_3HBNHR = H_2 + CH_3BNR$$

$$H_2BNH_2 = H_2 + HBNH$$

$$(CH_3)_2BNH_2 = CH_4 + CH_3BNH, \text{ etc.}$$

So far, only one borazine was separated: the monomeric $C_6H_5NBCH_3$, a colorless liquid, the properties of which are not known.

Other monomeric borazines appear to be hypothetical. They are obtained only as trimers of borazole, and of its alkyl derivatives. Their generalized formulas are:

$(HBNR)_3$ $(HBNH)_3$

$(CH_3BNR)_3$ $(CH_3BNH)_3$.

Borazole $B_3N_3H_6$ [43] is prepared by heating diborane, or tetraborane ammoniates in a closed vessel, at 180 — 190°:

$$3\ B_2H_6 \cdot 2NH_3 \longrightarrow 2\ B_3N_3H_6 + 12\ H_2$$

$$3\ B_4H_{10} \cdot 4NH_3 \longrightarrow 4\ B_3N_3H_6 + 21\ H_2 .$$

This reaction is accompanied by side reactions which decrease the yield of the borazole, and result in by-products. Formation of borazole can be represented by the equation:

$$3\ B_2H_6 + 6\ NH_3 \xrightarrow[2\ -\ 3\ \text{hours}]{180^\circ} 0.67\ B_3N_3H_6 + 4.05\ H_2 + 4.05\ BNH_{1,13}$$

from which, besides borazole, we obtain a white solid substance of the composition: $BNH_{1,13}$ and hydrogen. At a lower temperature of decomposition, e.g., 150° , 17 percent of diborane is converted into borazole, and 83 percent forms a white, solid, nonvolatile substance $BNH_{3,36}$, which is richer in hydrogen than borazole. We can show it in the equation:

$$3\ B_2H_6 + 6\ NH_3 \xrightarrow[\text{2-3 hours}]{150^\circ} 0.34\ B_3N_3H_6 + 7.8\ H_2 + 5\ BNH_{3,36}\ .$$

The yield of borazole doubles when the reaction is conducted at 180 — 190 and for 2 — 3 hours. The same yield will be obtained in 15 min, but the amount of hydrogen, and the composition of the solid will vary:

$$3\ B_2H_6 + 6\ NH_3 \xrightarrow[\text{15 min}]{180^\circ} 0.64\ B_3N_3H_6 + 6.95\ H_2 + 4.07\ BNH_{4,19}\ .$$

The maximum yield of borazole reaches 41 percent when diborane plus ammonia are heated at 200 — 220° for 45 min. Rapid increase of the temperature to optimum appears to be the necessary condition for a good yield.

Effect of the conditions of the reaction on the borazole yield [12].

Table 33

Pressure, atm	Temperature of reaction,	Time of reaction	Molar ratio $B_2H_6 : NH_3$	Yield of borazole, %
1	190	3 days	1 : 9	-
1	400	2 hours	1 : 9	-
1	150	2 - 3 hours	1 : 2	17
1	180	15 min	1 : 2	32
1	180 - 190	2 - 3 hours	1 : 2	33
1	200 - 220	45 min	1 : 2	41
5	200	20 min	1 : 2	23

The table shows that a pressure increase to 5 atm does not have a good effect on the formation of borazole. In this case the yield drops from 41 to 23 percent due to the formation of a solid residue, and the reaction is:

$$3\ B_2H_6 + 6\ NH_3 \xrightarrow[\text{20 min}]{200^\circ,\ 5\ \text{atm}} 0.36\ B_3N_3H_6 + 13.8\ H_2 + 5.98\ BNH_{1,27}$$

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In case of preparing borazole directly from a mixture of ammonia with a borane, an excess of ammonia over the amount necessary for the formation of the ammoniate will lead to the formation of by-products, e.g., boron imide, and boron nitride:

$$B_2H_6 + 6\ NH_3 \longrightarrow 2\ B(NH_2)_3 + 6\ H_2\ ,$$

$$B(NH_2)_3 \longrightarrow BN + 2\ NH_3$$

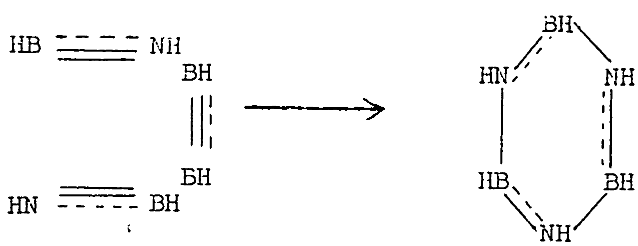
A ninefold excess of ammonia at 190° gives 80 percent boron imide and 9 percent boron nitride. At 400° the yield of boron nitride reaches 35 percent.

The following mechanism is proposed for the formation of borazole from diborane and ammonia:

$$B_2H_6 \cdot 2\ NH_3 \longrightarrow 2\ H_3\overset{-}{B} : \overset{+}{N}H_3 \qquad \text{"inorganic ethane"}$$

$$H_3\overset{-}{B} : \overset{+}{N}H_3 \longrightarrow H_2B \text{ ------ } NH_2 + H_2 \qquad \text{"inorganic ethylene"}$$

$$H_2B \text{ ------ } NH_2 \longrightarrow HB \equiv NH + H_2 \qquad \text{"inorganic acetylene"}$$



borazole, "inorganic benzene".

The first stage, during heating, dissociates the diamoniate into borine ammonia, a compound similar in structure to ethane. The second stage shows dehydrogenation of borine ammonia with the formation of a compound similar to ethylene. This compound is dehydrogenated in the third stage into "inorganic acetylene", and just as acetylene forms benzene when heated, it gives borazole, the I"inorganic benzene", from the trimerization of the last intermediate product.

Although the intermediate product borine ammonia $H_3\overset{-}{B} : \overset{+}{N}H_3$ was not separated, diborine and trimethylamine give an analogous compound, borine trimethylamine $H_3\overset{-}{B} : \overset{+}{N}(CH_3)_2$. Abundant generation of hydrogen points to dehydrogenation of intermediate products, which supports the proposed scheme of reaction.

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Another method was proposed, with the use of lithium borohydride and ammonium chloride:

$$3\ LiBH_4 + 3\ NH_4Cl \longrightarrow B_3N_3H_6 + LiCl + 9\ H_2.$$

A preliminary synthesis of boranes is not necessary. The reaction is conducted by heating the mixture of the two reagents $LiBH_4$ and NH_4Cl to about 300°.

The mechanism of this reaction shows that ammonium chloride dissociates when heated, into ammonia and hydrogen chloride:

$$6\ NH_4Cl \longrightarrow 6\ NH_3 + 6\ HCl.$$

The action of hydrogen chloride on the borohydride liberates diborane:

$$LiBH_4 + 6\ HCl \longrightarrow B_2H_6 + 6\ LiCl + 6\ H_2.$$

Diborane and ammonia yield borazole:

$$3\ B_2H_6 + 6\ NH_3 \longrightarrow 2\ B_3N_3H_6 + 12\ H_2.$$

Metal borohydrides are now produced in large quantities, so that borazole can be manufactured in considerable amounts from $LiBH_4$ and NH_4Cl. The advantage of substituting $LiBH_4$ with a borohydride of another, more available metal is obvious.

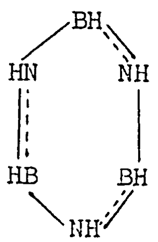
The yield of borazole is hindered by intermediate reactions. For instance, NH_4Cl reacts with borazole to form halo derivatives of borazole.

Effect of the conditions on the borazole yield [12].

Table 34

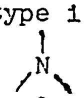
Quantity, moles		Temperature °C	Time of reaction, min	Yield of borazole, %
$LiBH_4$	NH_4Cl			
0.243	0.485	285	30	25.7
0.188	0.374	275	30	32.1
0.80	0.11	300	20	35.0
0.46	0.47	300	20	25.0

Trimerization of borazines permits various molecules to enter the reaction. In this way, the theoretical amount of possible alkyl derivatives of borazole is considerably greater.



Borazole and its derivatives have a benzenelike structure:

The double bonds are formed at the expense of the coordinate saturations of B and N atoms. The bond type is similar to that in NH_3:

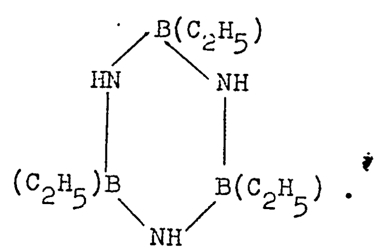


and the valence angle is plane, and equals 120° [45]. Recent studies show that borazole starts to decompose at room temperature, in absence of humidity in air, and in a few days gives H, B_2H_6, and solid polymers [50]. Decomposition was observed already at -80°.

Several of the organic borazole compounds were studied by various authors; Schlesinger synthetized B-trimethylborazole, and Wiberg achieved the synthesis of B-trimethylborazole. Zhigach, Kazakova, and Krongauz [17] prepared B-triethylborazole. So far, there was no mention in literature of B-ethylborazoles with radicals at the boron atom.

The thermal decomposition of triethylboron amine was selected for the preparation of triethylborazole:

$$3\ B(C_2H_5)_3\ NH_3 \xrightarrow{440\ -\ 450^{\circ}}$$



The best yield of 80 percent was obtained at 440 - 450° in an autoclave under pressure of 50 atm. Several other products with higher and lower boiling points were prepared at the same time. Here we find other ethyl derivatives of borazole.

Pure triethylborazole $(C_2H_5)_3B_3N_3H_3$ was collected at 66 - 67° in the amount of 33.0 g, which corresponds to a yield of 70 percent from the theoretical.

Quantitative analysis of triethylborazole [17].

Table 35

% %	B	N	C	H
Experimental	19.0 19.5	24.9 25.1	44.28 44.5	10.65 10.90
Calculated	19.72	25.5	43.76	11.02

It can be assumed that impure triethylborazole contains small admixtures of the initial product, borazole, mono- , di- , and hexaethylborazoles.

Triethylborazole $(C_2H_5)_3B_3N_3H_3$ is a mobile liquid at room temperature, which evaporates without residue. Density $d_4^{20} = 0.866$

viscosity $\nu_{20} = 1.48$ centistokes

fp = ca -54.

It does not react with water at room temperature, but hydrolyzes completely when boiled with 0.5 N hydrochloric acid for a longer time. Heated to 100° at normal pressure, it decomposes, forming gaseous products. Dissolves well in benzene, ether, ethyl alcohol, and acetone.

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Properties of borazole and of its derivatives [19].

Table 36

	Melting p. °C	Calculated boiling p. °C
$B_3N_3H_6$	-56.1	53
$NCH_3B_3B_3H_5$	-	84
$B,N(CH_3)_2B_3N_3H_4$	-	124
$N,N(CH_3)_2B_3N_3H_4$	-	108
$N,B,B(CH_3)_3B_3N_3H_3$	-	139
$N,N,N(CH_3)_3B_3N_3H_3$	-	134
$N,B,B,B(CH_3)_4B_3N_3H_2$	-	158
$N,N,N,B,B,B(CH_3)_6B_3N_3$	97.1	221
$N,N,N(C_2H_5)_3B_3N_3H_3$	-49.6	184
$N,N,N(n\text{-}C_3H_7)_3B_3N_3H_3$	vitreous	225
$N,N,N(iso\text{-}C_3H_7)_3B_3N_3H_3$	-6.5	203
$B,B,B(CH_3)_3B_3N_3H_3$	31.8	127
$B(CH_3)B_3N_3H_5$	-59	87
$B,B(CH_3)_2B_3N_3H_4$	-48	107

Diborane compounds with hydrazine.

Diborane reacts with hydrazine [12] as with other substances of basic character. The following compounds can be expected from this interaction:

$$H_3B : NH_2 — NH_2 \quad \text{and} \quad H_3B : NH_2 — NH_2 : BH_3$$

B 36.7% , N 46.8%, H 16.5% B 24%, N 61%, H 15%.

In case of a reaction of hydrazine with an excess of diborane at 0^o, and during 30 hours, the product is a white, solid, hygroscopic substance with the following composition: B 32.6 percent, N 52.0 percent, and H 14.4 percent, that is, it corresponds to the empirical formula: $BN_{1,2}H_{4,8}$.

The formation of this solid is accompanied by the generation of hydrogen. The solid is nonvolatile, and does not dissolve in ordinary solvents, e.g., ether, benzene, acetone, carbon tetrachloride, ethyl acetate, and also not in hydrazine and liquid ammonia. When heated, it detonates in air.

The product of the interaction of diborane with hydrazine is probably a mixture of both theoroetical products. When the solid is heated in vacuum to 180 — 200^o for 2 — 3 hours, it results in hydrogen and a solid residue. The solid taken for thermal treatment had the composition $BN_{1,26}H_{4,92}$ and it gave a solid substance with a lesser hydrogen content: $BN_{1,26}H_{2,81}$.

Other diborane N-compounds [19].

There are two groups of the other known N-compounds of diborane and N-nonbases: A) products of borine addition to methyl cyanide CH_3CNBH_3, white, nonvolatile, with low stability

B) product of the interaction of diborane with hydrazoic acid, the boron azide $B(N_3)_3$.

The white explosive $B(N_3)_3$ is formed at low temperatures according to the equation:

$$BH_3BH_3 + 6\ HN_3 \longrightarrow 2\ B(N_3)_3 + 6\ H_2.$$

Not so well known are other mixed derivatives of diborane, for instance, $NH_3B_2H_5PH_3$ which is formed from phosphinoborine, fluid ammonia, and $(CH_3)_3NBH_2SCH_3$.

Methods for the preparation of diborane N-derivatives [19].

Basic initial products for the preparation of N-derivatives of diborane are: diborane, and its methyl derivatives, and the corresponding nitrogen compounds, ammonia and amines. Their tendency to easy oxidation, often with ignition and explosion, and to hydrolysis, require safety measures, and high vacuum apparatus, which allows the preparation only of very small quantities of a substance. Relatively large quantities were synthesized in a flow of inert gas and at normal pressure.

The general method for the preparation of borazanes is based on the interaction of diborane and of its methyl derivatives with ammonia and amines. The reaction is very vigorous, evolving heat, and is normally conducted at low temperatures, -40 to -90°, to avoid thermal conversion of formed borazanes.

Borazanes with thermal stability, e.g., $BH_3N(CH_3)_3$, $BH_3NC_5H_5$, are prepared from the reaction of a metal borohydride with a salt of the corresponding amine, with a solvent added(ether, pyridine):

$$MeBH_4 + N(CH_3)_3HCl \longrightarrow MeCl + N(CH_3)_3BH_3 + H_2 .$$

The method is convenient because it uses available initial compounds, and the synthesis is performed by means of ordinary laboratory equipment. The reaction occurs at room temperature, and the yield is 80 — 90 percent from the theoretical.

Borazenes are prepared from the thermal conversion of borazanes, or by heating diborane and its derivatives with ammonia and corresponding amine. A slow heating of borazane to the required temperature leads to the formation of the corresponding borazene. The volatility of borazenes makes their separation easy by distillation in vacuum. Borazanes, which form in the reaction of trimethylboron with ammonia and amines, are used for the preparation of borazene B-derivatives: A variation of this method is found in the use of a metal borohydride and a salt of a secondary amine. It is based on the formation of borazane and its subsequent decomposition:

$$MeBH_4 + NHR_2HCl \longrightarrow MeCl + NHR_2BH_3 + H_2 ;$$

$$R_2HNBH_3 \longrightarrow R_2NHB_2 + H_2$$

The first reaction is conducted at room temperature, and with the addition of ether to the reagents. The decomposition of borazane takes place after the elimination of ether. The product obtained is dimethylaminoborine $N(CH_3)_2BH_2$ with a yield of up to 90 percent.

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Certain borazenes can be prepared from the products of thermal conversion of complex boron trichloride compounds with ammonia and amines. The borazene $(CH_3)_2NB(CH_3)_2$ was obtained by the alkylation of $[(CH_3)_2N]_2BCl$ with dimehtylzinc $Zn(CH_3)_2$. Here, together with the borazene $(CH_3)_2NB(CH_3)_2$, the compound $[(CH_3)_2N]_3B$ is also formed:

$$[(CH_3)_2N]_2BCl \xrightarrow{Zn(CH_3)_2} [(CH_3)_2N]_2BCH_3 \ ;$$

$$2\ [(CH_3)_2N]_2BCH_2 \longrightarrow [(CH_3)_2N]_3B + (CH_3)_2NB(CH_3)_2 \ .$$

Polymeric (BH_2NH_2) was prepared from lithium amide and diborane in ether, at -65°:

$$B_2H_6 + LiNH_2 \longrightarrow LiBH_4 + NH_2BH_2 \ .$$

$(NH_2BH_2)_x$ precipitates as a white powder.

Silylaminoborine is prepared from diborane monobromide and trisilylamine according to:

$$2\ B_2H_5Br + 2\ (SiH_3)_3N \longrightarrow 2\ SiH_3Br + B_2H_6 + 2\ (SiH_3)_2NBH_2.$$

The general method for the preparation of borazole and of its alkyl derivatives is the thermal conversion of borazenes with two H atoms at the nitrogen atom. Optimum conditions for the synthesis, pressure and temperature, were chosen for the preparation of several compounds. The initial materials used are: a metal borohydride and a salt of a primary amine. These compounds yield a borazane which is then used in the synthesis of N-alkyl derivatives of borazole.

Thermal treatment of $B_2H_6 2\ NH_2$ gives borazole and solids from side reactions. It results in the yield of only 35 percent from the theoretical, at 180°, the optimum temperature. N-alkyl derivatives of borazole show a yield of 80 — 90 percent.

Another method suggested the use of NH_4Cl and $LiBH_4$:

$$NH_4Cl + LiBH_4 \longrightarrow NH_3BH_3 + LiCl + H_2 \ ,$$

$$BH_3NH_3 \xrightarrow{-H_2} NH_2BH_2 \xrightarrow{-H_2} BHNH \ ,$$

$$3\ BNNH \longrightarrow (BHNH)_3 \ .$$

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The heating of NH_4Cl and $LiBH_4$ powders to 280 — 300° yields 30 percent borazole. Here, although polymerization occurs which lowers the yield of borazole, the interaction of borazole with NH_4Cl also takes place.

Mikheeva and Markina discuss this method and propose a way to increase the yield of borazole [17].

Authors propose the following scheme for the preparation of various products resulting from temperature increase during pyrolysis:

$$BH_3 + NH_3 \longrightarrow \underset{a}{BH_3 \cdots NH_3} \xrightarrow{-H_2} \underset{b}{BH_2 \overline{\cdots} NH_2} \xrightarrow{-H_2} \underset{c}{BH \overline{\overline{\cdots}} NH} \longrightarrow$$

$$\longrightarrow (- BH \overline{\overline{\cdots}} NH -)_3.$$

These compounds were named, by analogy to ethane, ethylene, and acetylene, as follows:

a = borazane
b = borazene
c = borazine.

Best yields of borazole, 47 percent of the theoretical, were obtained from the reaction of diborane with ammonia at 250 — 300°, with the pressure of one atm in the reactor, and with a ratio of reacting components $NH_3 : B_2H_6 = 2 : 1$. Preparation of pure borazole is made very complicated by the partial formation of diborane amine and diborane imide during the reaction.

Mikheeva and Markina selected the reaction of $LiBH_4$ with NH_4Cl as simplest in apparatus requirements and yielding a product of highest purity.

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Yield of borazole from the reaction of lithium borohydride with ammonium chloride [7].

Table 37

Experiment nr.	$LiBH_4$, g	NH_4Cl, g	Molecular ratio $\frac{NH_4Cl}{LiBH_4}$	Yield of borazole, %
1	1.0	2.46	1	10.70
2	1.0	2.46	1.1	10.80
3	1.1	4.70	1.7	13.8
4	1.0	4.7	1.9	20.80
5	0.93	4.7	2.0	19.60
6	1.45	7.5	2.12	20.7
7	0.76	4.7	2.4	17.2
8	0.64	6.0	3.7	16.9
9	0.7	3.6	2.09	33.8
10	1.09	5.0	1.97	36.59
11	0.72	3.6	2.03	37.3
12	0.50	2.5	2.09	38.1
13	0.50	2.45	2.0	38.4
14	0.73	3.5	1.94	41.70

Note: experiments 1 - 8 were conducted without stirring and without supplementary heating; experiments 9 — 14, with stirring

This reaction, carried out at a temperature of 300 — 350°, serves as a convenient method for the preparation of relatively pure borazole. While the pyrolysis of ammoniacal derivatives of di- and tetraborane, or the reduction of chlorine derivatives of diborane, do not give a pure product even after frequent distillations, the discussed method yields borazole of high purity already after 1 — 2 distillations.

It is interesting to note that there e:'sts a maximum yield of borazole at a definite ratio of the initial substances, slightly over the stoichiometry of the reaction, which requires an equimolecular ratio. This is shown in figure 3.

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This fact is evidently resulting from the heterogeneous character of the reaction, which hinders the equilibrium of the reaction. The fact of the existence of a maximum yield for a determined excess of ammonium chloride, and decrease of the yield in respect to lithium borohydride, regardless of the excess of ammonium chloride, can be explained only by the existence of a side reaction occuring in a great excess of ammonium chloride. Evidently, this will be the formation of chlorinated diborane and borazole, since in both cases, hydrogen tends to be substituted by chlorine in presence of HCl, which forms during the thermal dissociation of ammonium chloride.

The chemical analysis of borazole, and also its physical constants, m.p. -58.5°, vapor pressure 85 mm at 0° and 210 mm at 20°, are in agreement with data given by most reliable sources.

Storage of borazole in vacuum, and at room temperature, reveals a slight amount of hydrogen evolution which ceases after a certain length of time. This is probably due to the presence of traces of moisture adsorbed on the glass walls. Trace precipitation of a white substance after 5 — 6 months points to partial polymerization of borazole. It can be said that the high thermal stability of borazole is confirmed, and that it can be stored in complete absence of moisture.

Another method yielding 30 — 45 percent borazole [19] is based on the thermal processing of higher borane ammoniates, phosphinodiborane, and aminodiborane ammoniate:

$$B_5H_9 \cdot [illegible]\ NH_3,\ B_5H_{11} \cdot 4\ NH_3,\ B_4H_{10} \cdot 4\ NH_3,\ B_2H_6 \cdot PH_3NH_3,\ B_2H_5NH_2NH_3.$$

A recent method permits the preparation of borazole with yields to 65 percent, and in larger gram quantities [19]. The method is based on the reduction of B-trichloroborazole with lithium borohydride, in n-dibutyl ether as medium, and at room temperature:

$$B_3N_3H_3Cl_3 + 3\ LiBH_4 = B_3N_3H_6 + 1.5\ B_2H_6 + 3\ LiCl.$$

Details of the synthesis were not published, although the method was tested for the production of larger quantities of borazole.

<u>Diborane compounds with organic bases containing nitrogen.</u>

The first compounds to be discussed are the diborane derivatives of pyridine and quinoline [4].

Diborane reacts easily with substances which have molecules with electron-donor atoms. It behaves as if there were two BH_3 groups, which leads to the use of $(BH_3)_2$ instead of B_2H_6. Under ordinary conditions, diborane does not dissociate to form BH_3 groups, but it easily forms derivatives of this group with compounds which have the C(II), N, P, As, Sb, O, and S atoms. Other boranes in such a case also form compounds with the BH_3 group and polymeric addition products.

Complex compounds with the BH_3 group are of great theoretical interest. Besides the possibility of preparing new compounds and of accumulating new data, there is the possibility of clarifying the structure of boron hydrides and the nature of their bonds. Moreover, the chemistry of this class of compounds has practical meaning too, since almost all reactions involving boron derivatives reveal complexing in one of the intermediate stages of the reaction. Complex compounds with the BH_3 group may serve as a source of diborane, and as a reducing agent. This class of compounds can be useful in solving certain interesting problems of organic chemistry.

High reactivity of diborane with pyridine is used for the determination of the diborane yield in the reaction of lithium borohydride with the etherate of boron trifluoride in ether.

Pyridine and quinoline compounds with diborane were prepared by passing a stream of diborane through a layer of pyridine or quinoline, cooled by ice water, in a medium of dry nitrogen. The reactions can be shown as:

$$2\ C_5H_5N + B_2H_6 \longrightarrow 2\ C_5H_5N \cdot BH_3,$$

$$2\ C_9H_7N + B_2H_6 \longrightarrow 2\ C_9H_7N \cdot BH_3.$$

Yields of products are **quantitative** in relation to diborane. The diborane pyridine complex, after removal of the excess of pyridine in vacuum, is a colorless liquid with a characteristic odor. It dissolves in nitrobenzene, acetone, not so well in benzene, and poorly in ether. Its melting point is 9 — 10°, and according to Schlesinger et al. it is 10 — 11° (J.Am.Chem.Soc., 64, 325, 1942), and the temperature of decomposition is 155 — 160°.

Results of the analysis of the pyridine complex of diborane [4].

Table 38

	Percent of B	Percent of H act.	Percent of N	Ratio N: B : H act.
Compound obtained	11.29	3.10	15.50	1 : 1 : 3
For the composition: $C_5H_5N \cdot BH_3$	11.64	3.16	15.07	1 : 1 : 3

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The quinoline complex of diborane forms snow-white acicular crystals, with a faint quinoline odor, which in air, first turns yellow, then red. It dissolves very well in acetone, but does not dissolve in ether. Its melting point is 95 — 96°, and the decomposition temperature is 118°.

Results of the analysis of the quinoline complex of diborane [4].

Table 39

	Percentage of B	Percentage of H act.	Percentage of N	Ratio N : B : H act
Compound obtained	7.599	2.120	10.135	1 : 1 : 3
For the composition: $C_9H_7N \cdot BH_3$	7.578	2.102	9.804	1 : 1 : 3

Both these compounds show slow hydrolysis in water with generation of hydrogen. Hydrochloric acid in a ratio of 1 : 1 decomposes it completely:

$$C_5H_5N \cdot BH_3 + 3\,H_2O \xrightarrow{HCl} C_5H_5N + H_3BO_3 + 3\,H_2\uparrow .$$

According to results of analysis, diborane compounds with pyridine and quinoline have the following total compositions: $C_5H_5N \cdot BH_3$ and $C_9H_7N \cdot BH_3$.

Schlesinger and Burg (Chem.Revs, 31, 15, 1942) regard the pyridine compound of diborane as a monomer, by analogy with the trimethylamine compound with diborane, the molecular weight of which is determined from the composition $(CH_3)_3N \cdot BH_3$. But to draw such a conclusion in this case is not correct, since the donor capacity of a nitrogen atom in the $(CH_3)_3N$ molecule is several times greater than in pyridine, which is obvious even from the comparison of these compounds as bases. For $(CH_3)_3N$ $K = 5.27\ 10^{-5}$ and for C_5H_5N $K_b = 1.7\ 10^{-9}$,

The cryoscopic determination of the molecular weight of the pyridine complex with diborane, in nitrobenzene (table 39) and in benzene (table 40), performed by Mikheeva and Fedneva [4] indicates that the complex is a monomer when the concentration of the solution is of the order: 0.2 mol. percentage.

The degree of association, expressed by $\frac{M_{experimental}}{M_{theoretical}}$, increases with the increase of the concentration of the complex.

Molecular weight of $C_5H_5N \cdot BH_3$ ($M_{theoret.} = 99.92$) in nitrobenzene (K = 6.9)

Table 39 [4]

Quantity of complex, per mole	t °C	$M_{exper.}$	$\frac{M_{exper.}}{M_{theor.}}$
0.0022	0.123	99.8	1.00
0.0043	0.203	115.8	1.16
0.0067	0.319	119.2	1.19
0.0108	0.534	114.2	1.14
0.0336	1.332	146.9	1.47

Molecular weight of $C_5H_5N \cdot BH_3$ in benzene (K = 5.12)

Table 40 [27]

0.0017	0.134	95.9	0.96
0.0037	0.198	122.4	1.23
0.0058	0.246	277.2	2.77

The results of molecular-weight determination for the pyridine-diborane complex presented in a graph show clearly the change in the degree of association in relation to the concentration of the solution. The molecular weight increases slowly with the increase of concentration in a polar solvent, i.e., nitrobenzene. In benzene, a nonpolar solvent, it increases rapidly. These relations are shown in figure 4.

The diborane-pyridine compound appears to reveal association. Its solutions are partly dissociated, and the equilibrium of its various forms depends on the polarity of the solvent, and on the concentration of the substance in the solution:

$$(C_5H_5N \cdot BH_3)_{2n} \rightleftarrows \cdots \rightleftarrows n(C_5H_5N \cdot BH_3)_2 \rightleftarrows 2n(C_5H_5N \cdot BH_3).$$

The molecular weight of the quinoline complex with diborane was not determined due to the lack of a suitable solvent. The fact that quinoline seems to be a weaker base ($K = 6.3\ 10^{-10}$) than pyridine ($K = 1.7\ 10^{-9}$) presupposes the greater probability of its association of molecules.

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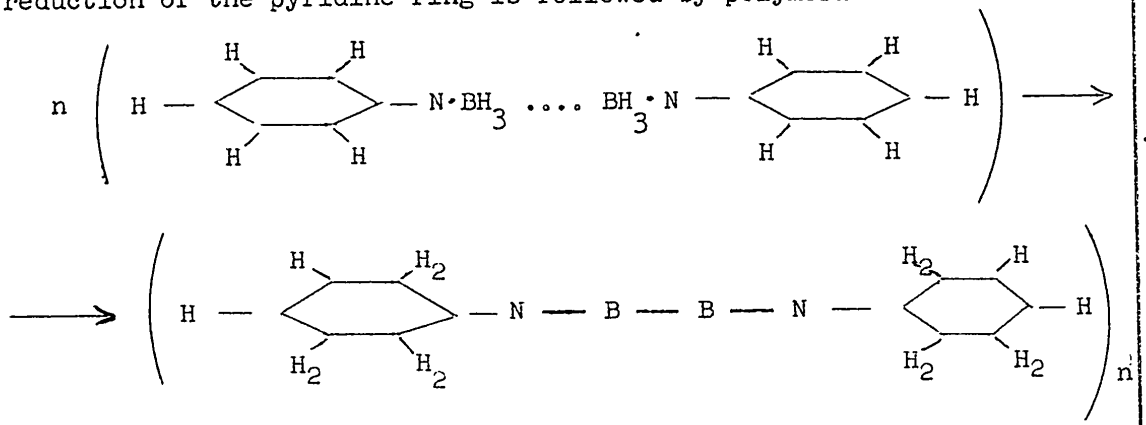
The pyridine complex forms a white flocculent sediment, without an appreciable evolution of gases, when standing in an open vessel. When standing with an addition of a small amount of lithium hydride, it converts into a yellow gelatinous mass which after pulverization shows a content of 0.2 percentage by weight. Hydrogen generation is not observed during the formation of the polymer. It is possible that a reduction of the pyridine ring is followed by polymerization:



Other reductions of this kind are mentioned in literature. For instance, the compound $CH_3CN \cdot BH_3$ when heated in a sealed tube gives a polymer composed of CH_3CH_2N — BH — elements. This transfer of hydrogen from the boron atom to the nearest carbon is so strong in liquid aldehydes and ketones that they practically do not form addition products.

It can be assumed that the hydrogen generation during acidic decomposition of the polymer occurs not due to the presence of active hydrogen in the molecule, but due to the B — B bonds of the polymer. The hydrolysis of the B — B bond can be shown as:

$$>B - B< \; + \; HOH \longrightarrow \; >B - H \; + \; HO - B<$$

$$>B - H \; + \; HOH \longrightarrow B - OH \; + \; H_2$$

The pyridine diborane complex when treated with $BF_3 \cdot (C_2H_5)_2O$, or with $AlCl_3 \cdot (C_2H_5)_2O$ liberates diborane. A double exchange reaction takes place between the two complex compounds. The stronger complexing agents BF_3 and $AlCl_3$ displace B_2H_6 from the compound:

$$2\ C_5H_5N \cdot BH_3 \; + \; 2\ BF_3 \cdot (C_2H_5)_2O \longrightarrow B_2H_6\uparrow \; + \; 2\ C_5H_5N \cdot BF_3 \; + \; 2\ (C_2H_5)_2O.$$

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It is possible that simultaneously with the formation of diborane the reduction of the pyridine ring occurs, and the formation of nonvolatile boron hydrides. The residue, as is the rule, contains active hydrogen.

Yield of diborane from the pyridine complex treated with BF_3 and $AlCl_3$ etherates [4].

Table 41

$C_5H_5N \cdot BH_3$	$BF_3 \cdot (C_2H_5)_2O$	MeHal eth: $C_5H_5N \cdot BH_3$	Yield of B_2H_6, in %
4.9 g (0.05 moles) 4.0 g (0.04 moles)	8.0 g (0.06 moles) 12.4 g (0.09 moles)	1.2 : 1 2.2 : 1	57.1 65.0
	$AlCl_3(C_2H_5)_2O$		
4.1 g (0.04 moles)	10.0 g (0.06 moles)	1.5 : 1	50.0

The quinoline complex heated with methyl alcohol does not form a complex compound of quinoline with methylboron ether $C_9H_7N \cdot B(OCH_3)_3$ as it might be expected, but an azeotrope of the methylboron ether with methyl alcohol and quinoline:

$$C_9H_7N \cdot BH_3 + 3\ CH_3OH \xrightarrow{CH_3OH} 3\ H_2 + B(OCH_3)_3 .$$

The pyridine complex of BH_3 also reacts with methyl alcohol, only in this case pyridine is liberated.

As is known, the corresponding compounds of pyridine and quinoline with methylboron ether, could not be successfully prepared by the direct interaction of these compounds. Evidently, steric factors play the deciding role.

The second group of diborane compounds with N-containing organic bases includes compounds with aniline and dimethylaniline [5]. Diborane reacts with these compounds as an electron acceptor, and the nitrogen atom in the organic compound is the electron donor. The reaction is spontaneous and exothermic, as in the case of diborane interaction with pyridine and quinoline.

The reaction of diborane with aniline did not result in the compound: $C_6H_5NH_2 \cdot BH_3$. Saturation of aniline with diborane is connected with the liberation of gaseous hydrogen. The precipitate is a white, acicular substance, extremely hygroscopic, well soluble in aniline and poorly soluble in ether. The analysis of the compound shows a composition close to $(C_6H_5)_2N_2N_2BH$:

Table 42 [5]

	$H_{act.}$, %	B, %	N, %	
$(C_6H_5)_2N_2H_2 \cdot BH$	0.49	5.36	13.80	experimental
	0.51	5.55	14.10	calculated

The proposed formula for this compound is $(C_6H_5NH)_2BH$, and it is regarded as a borine derivative. The second general formula for this composition is the structural presentation $C_6H_5N = BH \cdot C_6H_5NH$ with a crystalline aniline molecule. This formula should be rejected, since even prolonged drying in vacuum, 3 — 5 mm Hg at 50°, does not reveal the liberation of the aniline molecule.

The interaction of diborane with aniline, in the presence of excess of aniline, shows the following stages: first of all, there is the possibility of the formation of the addition product $C_6H_5NH_2 \cdot BH_3$ which liberates gaseous hydrogen from the hydride group linked with boron, and from protonic hydrogen linked with nitrogen:

$$[C_6H_5NH \cdot BH_3] \xrightarrow{-H_2} C_6H_5NH - BH_2 \xrightarrow{C_6H_5NH_2} C_6H_5NH - BH_2 \cdot C_6H_5NH_2 \xrightarrow{-H_2}$$

$$\xrightarrow{-H_2} (C_6H_5NH)_2BH \text{ etc.}$$

With relatively large quantities of diborane, the reaction can lead to the formation of other compounds, such as $C_6H_5 = BH$, and borazole derivatives, tri-N-triphenylborazole $(C_6H_5)_3N_3B_3H_3$.

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Dimethylaniline and diborane form dimethylanilineborine $C_6H_5N(CH_3)_2 \cdot BH_3$, a white crystalline substance. The composition is shown in table 43:

Table 43 [5]

	$H_{act.}$, %	B, %	N, %	
$C_6H_5N(CH_3)_2 \cdot BH_3$	2.25	8.16	11.07	experimental
	2.24	8.01	10.37	calculated

Its melting point is 35°, it is poorly soluble in ether, and extremely hygroscopic.

It is evident that hydrogen generation is characteristic for reactions of diborane with primary aromatic amines. This tendency to form hydrogen will vary for different aniline derivatives substituted in the nucleus.

As is known from literature, diborane reacts with primary and secondary aliphatic amines producing addition products $(CH_3NH_2)_2 \cdot B_2H_6$ and $(CH_3)_2NH \cdot BH_3$, which liberate hydrogen only when heated.

The tertiary aliphatic-aromatic amine (dimethylaniline) reacts with diborane and forms a borine derivative with a greater reactivity of the hydrogen atom in the hydride, which is possible due to spatial factors preventing the formation of strong donor - acceptor N — B bonds.

Application of diborane N-derivatives [19].

There is lack of data in literature due to insufficient progress in the study of these compounds.

It should be noted that the high reactivity of many of them, make possible their use as reagents, for the introduction of boron and nitrogen into various compounds.

They may also serve as reducing agents. Pyridineborine remains inert in neutral and alkaline media towards certain compounds, but acts as a strong reducing agent in acidic media.

Certain polymers are not soluble in any organic solvents, which is a very important feature in plastics in relation to oils and hydrocarbon fuels.

Some of the solid derivatives were tried out in rubber vulcanization, and also as cross-linking agents.

Pentaborane derivatives [18].

The literature does not mention reactions of alcohols and ketones with pentaborane. There are limited data on the interaction of alcohols and ketones with other boranes: diborane and tetraborane.

The following compounds were used in reactions with pentaborane: methyl, butyl, ethyl alcohols, and acetone. Experiments show that these reactions occur with the formation of intermediate compounds: alkoxyborines. The effect of small quantities of dehydrated alcohols on pentaborane is seen in partial evolution of hydrogen. Consecutive addition of alcohol liberates additional hydrogen. It is completed after the addition of 15 moles of alcohol for 1 mole of pentaborane. The final result is a boric ester and 12 molecules of hydrogen:

$$5\ ROH + B_5H_9 \longrightarrow 5\ BH_2(OR) + 2\ H_2 \qquad (1)$$

$$5\ ROH + 5BH_2(OR) \longrightarrow 5\ BH(OR)_2 + 5\ H_2 \qquad (2)$$

$$5\ ROH + BH(OR)_2 \longrightarrow 5B(OR)_3 + 5\ H_2 \qquad (3)$$

summary equation

$$15\ ROH + B_5H_9(OR)_2 \longrightarrow 5\ B(OR)_3 + 12\ H_2 \qquad (4)$$

Addition of alcohol to pentaborane in quantities corresponding to the summary equation, gives a reaction in the direction of the boric ester as well at room temperature, as after cooling to -20°, with intensive generation of heat. Methyl, ethyl, and butyl esters of boric acid were synthesized from the interaction of pentaborane with the corresponding alcohols. These esters were separated and analyzed.

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Results of the qualitative analysis [18].

Table 44

Compound	C, %		H, %		B, %		Yield of compound, %
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	
B_5H_9	-	-	14.3	14.36	85.5	85.64	-
$B(OCH_3)_3$	34.3 33.9	34.66	8.6 8.9	8.73	10.4 10.61	10.41	92
$B(OC_2H_5)_3$	48.9 49.6	49.30	10.15 10.3	10.36	7.43 7.36	7.41	95
$B(OC_4H_9)_3$	62.8 62.0	62.6	11.6 11.45	11.83	4.65 4.60	4.7	85
$B(i\text{-}OC_3H_7)_3$	57.34 57.50	57.5	11.45 11.33	11.26	5.48 5.65	5.72	-
$BH(OC_2H_5)_2$	-	-	1.01 0.97	0.98	10.77 10.48	10.62	40

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Physical properties [18]

Table 45

Compound	b.p., °C, at mm	m.p., °C	density	molecules per cm³	Reference
B_5H_9	60.0 – 60.2 760 mm	-46.5	d_4^{20} 0.625	-	
	58.1				D.R. Stell, Tables of vapor tension .. 1949, p. 57.
$B(OCH_3)_3$	68.0 – 69.5	-	d_4^{20} 0.928	n^{20} 1.352	
	67.7 – 67.8		d_4^{20} 0.932	n^{24} 1.3558...	W. Seaman, I.R. Johnson, J.Am.Chem.Soc., 53, 713, 1931.
$B(OC_2H_5)_3$	117.5 – 118.0 745 mm				
	118.3 – 118.4 740.5 mm				S.H.Webster, L.M. Dennis, J.Am.Chem. Soc., 55,3233,1933.
$B(OC_4H_9)_3$	236 – 239 750 mm	-	d_{27}^{27} 0.8553	-	
	234 – 238 745 mm		$d_{27.5}^{27.5}$ 0.856		F.R.Bean, I.R.Johnson, J.Am.Chem.Soc., 54,4416, 1932.
$B(i\text{-}OC_3H_7)_3$ ..	139 – 140	-	-	-	
	140°				C. Councler, Ber., 11, 1106, 1878.

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APPLICATIONS OF THE BORON HYDRIDES IN TECHNOLOGY

Rocket fuel.

A rocket engine, as any other type, needs a certain source of energy for its performance [3]. The only source of energy at the present is the chemical energy. This energy can be supplied in two ways. The first is the most common process of combustion. The second is the exothermic decomposition of certain substances. An example of this type is the wide use of hydrogen peroxide in rocket engines.

The combustion process means an interaction of two substances, the fuel and the oxidixing agent, which occurs with heat generation.

A considerable amount of heat is generated during the oxidation of a series of hydrides, e.g., beryllium hydride, or boron hydride [16]. Thermodynamic data show that the complete combustion of a mixture of borane and oxygen generates approximately twice as much heat as the same amount of a hydrocarbon-oxygen mixture. Such heat values, together with the high reactivity of many boranes, and of their derivatives, with water, renders them suitable as special fuels. For instance, as fuel for submarine rocket missiles.

Of all the elements, only oxygen and fluorine can be used as oxidizing agents which furnish a great quantity of chemical energy, and maintain the necessary intensity of combustion. The most effective fuels are the following elements: beryllium, lithium, boron, aluminum, magnesium, silicon, and carbon.

Properties of some basic fuels [1].

Table 46

Fuel	Phase	Mol. weight kg/l	Sp. gr	b.p. t_b °C	m.p. t_m °C
B	solid	10.82	1.73	-	2300
Li	solid	6.941	0.534	1400	180

So far, engines using metallic fuels are not yet developed, although metal - oxygen, and metal - fluorine fuels are discussed [20]. Metals give much higher heat effects than ordinary hydrocarbon fuels. Molecular weights of products of metal combustion, as a rule, are very high, what with great heat effects, leads to very high temperatures in the combustion chamber, and to considerable dissociation. The boiling points of fluorine products in the combustion of metals are considerably lower than those of oxygen compounds.

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Literature on rocket fuels discusses the ways and means of increasing the heat generation values of fuels [1]. This may be achieved by the use of components other than pure elements in standard form, that is such compounds which regardless of the chemical energy of elements freed in combustion, possess positive heats of formation. Efforts were made to introduce new oxidizing agents (ozone, fluorine and its compounds), and new fuels, suspensions of metals in kerosene, boron hydrogen compounds, and a series of metal organic compounds. But engines do not yet exist which would be able to use such fuels.

Metals can be used for the improvement of the heat generation of other fuels, and for the increase in specific gravity. [10]. These additives should have high heat generation and high specific gravities. As such we can list: beryllium, boron, aluminum, magnesium, and silicon. The method of G.A. TSander appears to be impractical because of: insufficient mixing, deposits on the inner walls of the chamber, entrailment of solid particles by gases, etc. ("Problema poleta pri pomoshchi reaktivnykh apparatov" G.A. TSander, 1932). These shortcomings are caused by the fact that the products of combustion include solid particles, and are not gaseous. Better results are obtained by the use of metallic fuels in the form of colloidal solutions in liquid fuels.

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Properties of combustion products /1/.

Table 47

Oxides	Phase	Mol. wt	$\Delta H^o_{298.16}$ kcal/g mole	K_G kcal/kg	ν_0 kg/kg	γ kg/l	K_V kcal/l	t_b ^oC	$H_{exp.}$ kcal/kg	Heat generation per 1kg of mixture (13)
B_2O_3	solid	69.64	-302.000	4350	2.21	1.28	5570	-	-	3900
Li_2O	solid	29.88	-142.400	4760	1.15	0.75	3570	1300	(1160)	4710
Fluorides										
BF	gas	67.82	-265.4	3910	5.26	1.21	4750	-101	-	
LiF	solid	25.94	-146.3	5650	2.74	0.87	4930	1680	(1960)	-

K_V = volumetric heat generation capacity

K_G = heat generation capacity

ΔH = heat of formation

ν = amount of oxidizer (kg) to 1 kg of fuel

γ = specific gravity of fuel

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Metals, which are considered as possible rocket fuels, are characterized by great heats of combustion [13]. The following table gives thermodynamic data of some fuels:

Table 48. [13]

Compound	Total weight $\varphi = 0.75$ $v = 7.55$ km/sec	Weight of metal oxidized	Heat generation	O_2, %	Theoretical velocity	Order nr. by weight of metal
Li_2O	4.98	1.85	4710	53.5	6270	2
LiF	5.82	2.33	4450	44.7	6100	7
B_2O_3	5.85	1.53	3900	68.5	5700	1
$Na_2B_4O_7$	6.14	2.24	3700	55.5	5550	6
gasoline	9.71	-	2350	77.5	4430	-

φ = coefficient for the decrease of velocity due to friction

v = flight velocity

The smallest total weight is shown for Li_2O, and the smallest amount of the solid needed for combustion is obtained when B_2O_3 is used. But boron will probably be used only in the form of a powder, amorphous boron, to form the insulation of the rocket, or as extruded rods of crystalline boron as structural elements. There is a possibility of a rocket carrying supercooled borane. But boron requires 68.5 percent O_2 of the weight of B_2O_3, which is a large amount, and may cause difficulties.

Lithium and boron appear to be the most suitable fuel components for jet engines in view of their low atomic weight, and consequently, their low consumption.

Fuel components are boosters when they are compounds which, regardless of the chemical energy of elements freed in combustion, possess positive heats of formation [1]. This heat is generated in combustion reactions and adds to the chemical energy of the products of combustion.

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Properties of certain metal-organic and metal-hydride compounds [1].

Table 49

Compound	m.p. °C	b.p. °C	heat of formation kcal/g mole	sp gr	Reference other than (1)
B_5H_9	(50)	(60)	(0)	(0.64)	
B_2H_7N	-66	76	(-10)	(0.70)	
$B_{10}H_{14}$	100	213	-	(0.28)	(20)
Si_3H_8	-117	53	(-20)	(0.88)	
$(SiH_3)_3N$	-106	52	(+10)	0.895	

( ) denotes doubtful value

Industrial use of boranes [16].

It was established that boranes and certain of their derivatives can be used in the vulcanization of polymers, including natural and synthetic rubber. The addition of some tenths of a percent of decaborane is as effective, as the addition of three percent sulfur. Certain rubbers vulcanized with boron hydrides are not inferior in their physical properties to rubbers vulcanized with sulfur, and sometimes are even better.

Decaborane is especially suitable for the vulcanization of organosilicon resins. It noticeably increases the thermal stability, and decreases the ageing tendency, without affecting the other physical properties of the polymers.

Decaborane can also be used for the gelation of poly(dimethyl) siloxane giving a rubberlike resin, and can be used in the vulcanization of such a resin.

Most of the volatile hydrides are highly toxic and serve as fumigants. Boranes are included in this group.

The low thermal stability of certain hydrides recommends them for coating metal and ceramic surfaces with the corresponding element. For instance, heated metal and ceramic surfaces in an atmosphere of volatile boranes, diborane, etc., are coated with a dense, smooth layer of elemental boron, which is extremely hard, and does not corrode at higher temperatures.

Coatings of thin boron films, obtained from diborane pyrolysis, are used in neutron counters.

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Boron coatings on metals, usually iron, are successfully used in making grinding bars, bearings, press moulds, and also as an intermediate layer in bonding ceramics to metal and graphite. A layer of boron on iron or steel protects the metal from oxidation at temperatures of 1000° and higher.

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(CLASSIFICATION)

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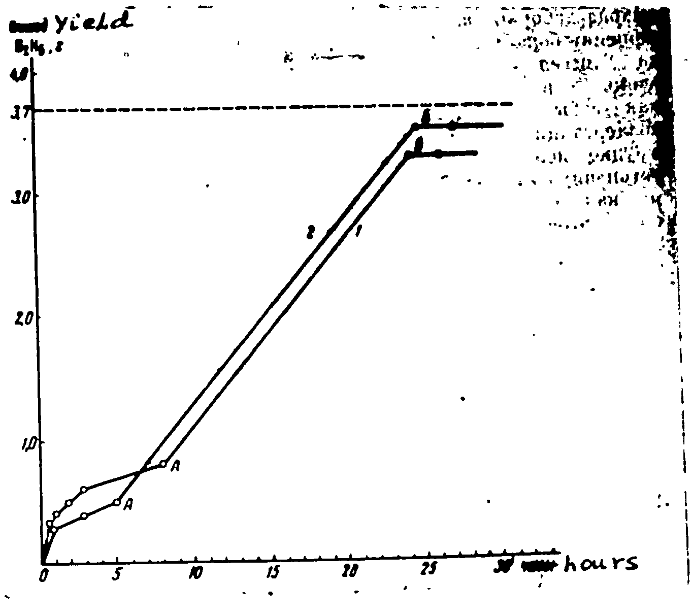

Fig. 1 - Time study of the generation of diborane:

1 - experiment nr. 3

2 - experiment nr. 4 .

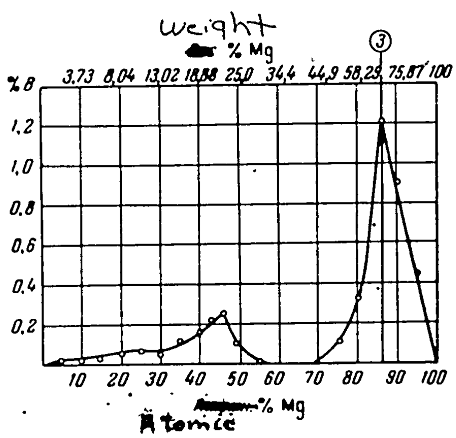

Fig. 2 - Yield of boranes from the baking of a mixture of magnesium and boric anhydride.

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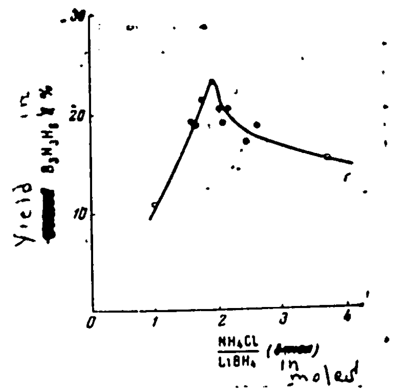

Fig. 3 - Effect of the ratio of ammonium chloride to lithium borohydride on the yield of borazole.

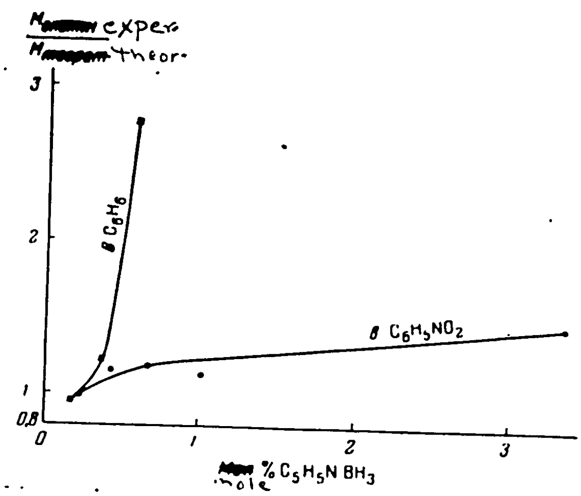

Fig. 4 - Molecular weights of $C_5H_5N{\cdot}BH_3$ in benzene and nitrobenzene.

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